

Dilute Solution Behavior of a Cationic Polyelectrolyte

CARLOS KIENZLE-STERZER, DOLORES RODRIGUEZ-SANCHEZ, and CHOKYUN RHA, *Biomaterials Science and Engineering Laboratory, Department of Nutrition and Food Science, Massachusetts Institute of Technology, Cambridge, Massachusetts*

Synopsis

Dilute solution behavior of a cationic polyelectrolyte was studied with respect to acetic acid concentration using chitosan. The reduced viscosity, η_{sp}/C , of chitosan solutions increases with a decrease in the polymer concentration. For a given polyelectrolyte concentration, the specific viscosity is higher at lower acid (acetic) concentration, indicating the expansion of the polyelectrolyte chain due to electrostatic repulsion as a result of the interactions between chitosan and the solvent. The relationship between intrinsic viscosity $[\eta]_0$ and acetic acid concentration suggests no conformational transition of the chitosan molecules and possible formation of intramolecular hydrogen bonds during the shrinking of the hydrodynamic domain of the polyions.

INTRODUCTION

Dilute solution behavior of a cationic polyelectrolyte was studied using chitosan (1-4, 2-amino-2-deoxy- β -D-glucan). Chitosan, an exception to current industrial or commercial high molecular weight hydrocolloids or polysaccharides which are all polyanionic, is insoluble in a neutral or alkaline aqueous solvent but soluble in dilute organic acids¹ and thus is a unique polymer with great potential application. Chitosan has been used for coagulation of protein, detection of ions, and in recovery of heavy metals.^{2,3}

This study describes the characteristic polyelectrolytic behavior of chitosan in dilute solutions.

EXPERIMENTAL

Chitosan (Madera, Madera Products Inc., Albany, Oregon) obtained from Tanner (Snow) crab (*Chionoecetes bairdi*) with 80% of deacetylation was used in this study. Chitosan solutions, 10^{-3} – 10^{-4} g/dL in dilute acetic acid (0.17 – $1.7 \times 10^{-3}M$) were prepared by stirring at room temperature until complete dissolution. The solution was allowed to rest for 24 h. The viscosity data were obtained with a Cannon-Fenske viscometer at 29°C. No shear correction was made.

RESULTS AND DISCUSSION

The reduced viscosity of uncharged polymers decreases linearly with decreasing polymer concentration following Huggins equation.⁴ This is not true for polyelectrolytes, where, at low ionic strength, the reduced viscosity increases with further dilution.⁵

Figure 1 shows the dependence of the reduced viscosity, η_{sp}/C , on chitosan

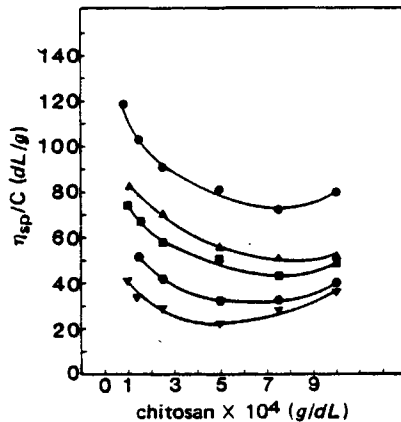


Fig. 1. Reduced viscosity (dL/g) vs. chitosan concentration (g/dL) at different acetic acid concentration: (●) $1.7 \times 10^{-3}M$; (▲) $8.3 \times 10^{-3}M$; (■) $1.7 \times 10^{-2}M$; (◈) $8.3 \times 10^{-2}M$; (▼) $1.7 \times 10^{-1}M$.

concentration. The reduced viscosity increases with a decrease in polyelectrolyte concentration below 10^{-3} g/dL. Figure 1 also shows the reduced viscosity-concentration relationship with respect to the acid concentration in solution. The increase in reduced viscosity at low chitosan concentrations (observed in all cases) is progressive at low acid concentrations. The increase starts to occur at high polyion concentration as the concentration of acid in solution decreases. Moreover, these reduced viscosities are higher at lower acid concentration in all cases. The increase in reduced viscosity is believed to be due to the expansion of the backbone caused by greater Coulombic repulsion forces between the charged points, which results from the decreased shielding of fixed charges on polyions.⁶

The increase in reduced viscosity at near zero concentration makes the extrapolation to zero concentration no longer possible. Therefore, the intrinsic viscosity of the chitosan solutions, $[\eta]$, cannot be obtained by the usual method of extrapolation to zero concentration.

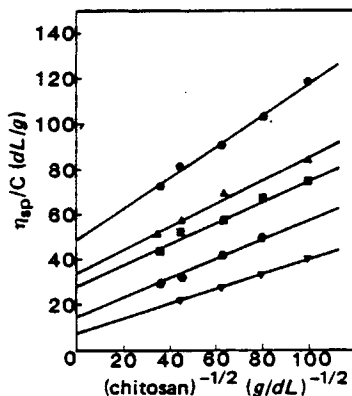


Fig. 2. Reduced viscosity (dL/g) vs. the reciprocal of the square root of chitosan concentration $(g/dL)^{-1/2}$ at different acetic acid concentration: (●) $1.7 \times 10^{-3}M$; (▲) $8.3 \times 10^{-3}M$; (■) $1.7 \times 10^{-2}M$; (◈) $8.3 \times 10^{-2}M$; (▼) $1.7 \times 10^{-1}M$.

TABLE I

Acetic acid concn (M)	$[\eta]_{\infty}$ (dL/g)	K (g/dL) ²	Corresponding coefficient
1.7×10^{-3}	48.60	1.43×10^{-2}	0.9935
8.3×10^{-3}	32.56	1.51×10^{-2}	0.9921
1.7×10^{-2}	27.22	1.70×10^{-2}	0.9917
8.3×10^{-2}	12.57	3.46×10^{-2}	0.9933
1.7×10^{-1}	6.46	4.71×10^{-2}	0.9952

In order to describe the anomalous concentration dependence of the reduced viscosity, several semiempirical equations may be used.⁷⁻¹⁰ The following equation,¹⁰

$$\eta_{sp}/C = [\eta]_{\infty}(1 + KC^{-1/2})$$

was used to represent our experimental data. The parameter $[\eta]_{\infty}$ has been related to the intrinsic viscosity $[\eta]$ in salt solution and K to the effects of electrostatic interaction between the polyion and the solvent. This relationship between $[\eta]_{\infty}$ and $[\eta]$ in salt solution has been shown to apply to heparin solutions of molecular weight in the range of 6000–16000 daltons¹⁰ and in sodium carboxy-methylcellulose solutions.¹¹

A straight line was obtained when reduced viscosity was plotted against the reciprocal of the square root of chitosan concentration according to the above equation (Fig. 2). The values of $[\eta]_{\infty}$ and K and the linear correlation coefficient for the experimental values were obtained using linear regression analysis (Table I) where the values for $[\eta]_{\infty}$ at high acetic acid concentration are similar to the reported values of $[\eta]$ for chitosan solutions obtained at values of the reciprocal of the square root of the ionic strength between 1 and 7 using KCl.¹² The decrease in $[\eta]_{\infty}$ at higher acetic acid concentration suggests that some of the charges on the polyion have been neutralized by the acetic ions, leading to increased flexibility of the local chain, which in turn causes the macroion domain to shrink, consequently decreasing the intrinsic viscosity.⁶ The evidence of an increase in the interaction between the polyelectrolyte and the counterions as acetate concentration increases is shown by the higher K values at increased acid concentration (Table I).

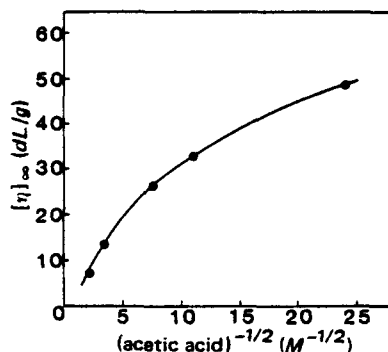


Fig. 3. Intrinsic viscosity $[\eta]_{\infty}$ (dL/g) vs. the reciprocal of the square root of the acetic acid concentration ($M^{-1/2}$).

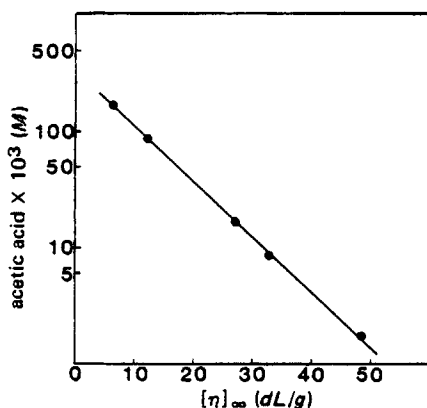


Fig. 4. Logarithm of the acetic acid concentration vs. intrinsic viscosity $[\eta]_{\infty}$ (dL/g).

Given that the acetic acid acts both as a solvent and as a simple electrolyte when added to the chitosan solution, a linear relationship is expected between $[\eta]_{\infty}$ and the reciprocal of the square root of the acetic acid concentration.^{13,14} However, when $[\eta]_{\infty}$ is plotted against the inverse of the square root of the acetic acid concentration (Fig. 3), deviation from linearity is observed. This effect can be attributed to an increase in intramolecular hydrogen bonds caused by shielding of the electrostatic repulsive forces as acetic acid concentration increases, thus favoring the shrinking process.^{15,16} Furthermore, the linear relationship between $[\eta]_{\infty}$ and the logarithm of acetic acid concentration (Fig. 4) indicates that there is no conformational transition of the chitosan molecules during the shrinking process under the experimental conditions.

This study was supported by M.I.T. Sea Grant No. 90879, "Synthesis of Chitosan Structure Matrix for Food," from NOAA Department of Commerce, Office of Sea Grant, NA79AA-D-00-101, with partial support provided by C.O.N.I.C.I.T., Caracas, Venezuela, to Carlos A. Kienzle-Sterzer. The authors wish to thank Robin Hoe for her technical support.

References

1. R. A. A. Muzzarelli, *Chitin*, Pergamon, Oxford, 1977.
2. W. A. Bough, *Poultry Sci.*, **54**, 1904 (1975).
3. M. S. Masri, F. W. Reuter, and M. Friendman, *J. Appl. Polym. Sci.*, **18**, 675 (1974).
4. M. L. Huggins, *J. Am. Chem. Soc.*, **64**, 2716 (1942).
5. C. Wolff, *J. Physique, Colloq.*, **C2**, 169 (1978).
6. H. W. Chien, C. H. Isihara, and A. Isihara, *Polym. J.*, **3**, 288 (1976).
7. R. M. Fuoss, *J. Polym. Sci.*, **3**, 603 (1948).
8. P. A. Liberti and S. S. Stivala, *J. Polym. Sci., Part B*, **4**, 137 (1966).
9. J. R. Schaeffgen and C. F. Trivisonno, *J. Am. Chem. Soc.*, **74**, 2715 (1952).
10. L. Yuan, T. J. Dougherty, and S. S. Stivala, *J. Polym. Sci., Part A2*, **10**, 171 (1972).
11. H. C. Trivedi, C. K. Patel, and R. D. Patel, *Angew. Makromol. Chem.*, **95**, 155 (1981).
12. A. I. Gamzazade, A. M. Sklyar, S. S. A. Pavlova, and S. V. Rogozhin, *Visokomol. Soedyn. Ser. A*, **23**, 594 (1981).
13. A. Takahashi and M. Nagasawa, *J. Am. Chem. Soc.*, **86**, 543 (1964).
14. N. Ohno, K. Nitta, S. Makino, and S. Sagai, *J. Polym. Sci., Part C*, **11**, 413 (1973).
15. I. Noda, T. Tsuge, and M. Nagasawa, *J. Phys. Chem.*, **74**, 710 (1970).
16. R. Yen and A. Isihara, *J. Polym. Sci., A-1*, **8**, 861 (1970).

Received December 11, 1981

Accepted June 7, 1982