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DETERMINATION OF INTRINSIC VISCOSITIES AND MARK-HOUWINK-SAKURADA CONSTANTS FOR SODIUM ALGINATES

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Introduction

The islands of the Caribbean have been affected by an influx of Sargassum natans on their beaches (Hotel 2015). This influx creates a wide range of problems for fishermen and their livelihoods as it results in complications in launching boats, restricts access to fishery resources and lastly, they decompose to give a very foul smell, thus affecting tourism.

Sodium Alginate may be extracted from the cell walls of Sargassum natans (Mohammed et al. 2018), and its derivatives have many useful applications in a number of areas including the chemical, cosmetic, medical fields and also as a bio-absorbent of heavy metal ions in wastewater treatment. In modelling this absorption, a knowledge of the molecular weight (M_w) of the alginate would aid in the understanding of the interaction between the monomers of the alginate and the heavy metal ions. M_w may be found by firstly determining the intrinsic viscosity, $[\eta]$ of the alginate and applying the Mark-Houwink-Sakurada (M-H-S) equation which correlates $[\eta]$ and M_w.

The objectives of this work are three-fold. Firstly, to determine the applicable concentration range to be considered for determination of $[\eta]$ of sodium alginates using the multi-point dilution method. Secondly, to determine the $[\eta]$ of four sodium alginates – one extracted from Sargassum natans obtained from the East Coast of Trinidad and three commercial (Sigma-Aldrich, Manugel LBA and Protanal LF) using both the multi-point dilution method and two, single-point methods. Thirdly, to determine the constants in the M-H-S Equation for alginates of this particular M_w size range using independently obtained M_w's for the four alginates (obtained previously via Gel Permeation Chromatography, GPC)

The significance of this work is that once the M-H-S constants are known, the values of the M_w of the alginates may be determined via dilute solution viscometry rather than more detailed and expensive methods such as GPC.

Materials and Methods

Between 0.015 and 0.65 g of commercial Protanal LF Sodium Alginate was dissolved in 100 mL 0.1 M NaCl solution. 10 mL of solution was charged to Size OB Ubbelohde viscometer placed in a Cannon CT 600 Constant Temperature Bath. Efflux times were repeatedly measured until consistent readings were obtained as per ISO (2019). Two subsequent insitu dilutions were made each with 5 ml of the NaCl solution and efflux times measured. This procedure was repeated using 0.1 g of Sodium Alginate extracted from Sargassum natans obtained from the East Coast of Trinidad and from two other commercial Sodium Alginates (Sigma-Aldrich and Manugel LBA).

Theory

The M-H-S equation relates $[\eta]$ (which is a measure of a solute's contribution to the viscosity, η of a solution) and M_w, according to (Rudin and Choi 2012)

$$[\eta] = K\, M_w^a$$

$[\eta]$ can be determined by extrapolating plots of reduced, η_{red} and inherent, η_{inh} viscosities versus concentration C to infinite dilution according to

$$\lim_{c\to 0}(\eta_{inh}) = \lim_{c\to 0}\left(\frac{\ln \eta_r}{C}\right) = \lim_{c\to 0}\left(\frac{\eta_i}{C}\right) = [\eta] = \lim_{c\to 0}(\eta_{red})$$

where η_r and η_i are the relative viscosity and relative viscosity increment respectively (all of these viscosities are related to ratios of η for the solution to that of η for the solvent.

The efflux time t for a liquid through a capillary tube viscometer is related its viscosity η by the Poiseuille-Hagenbach-Couette Equation (ISO 2019)

$$\frac{\eta}{\rho} = C't - \left(\frac{A}{t^2}\right)$$

For the same viscometer, at fixed temperature and pressure, suitable choice of viscometer bore and solution concentration, the ratio of η for a solution and its solvent is given simply by the ratio of t for the solution and for the solvent. If however the range of concentrations measured is too high, then the density ρ for the solution and for the solvent will differ. If the concentration range is too low there may be absorption of polymer on the capillary wall. These factors could cause plots of η_{red} and inherent, η_{inh} to curve away from the C axis and the extrapolation would no longer be linear (Rudin and Choi 2012)

$[\eta]$ may also be determined using single-point methods such as (Rudin and Choi, 2012)

$$[\eta] = \frac{0.25(\eta_r - 1 + 3\ln \eta_r)}{C} \qquad [\eta] = \frac{[2(\eta_r - 1 - \ln \eta_r)]^{1/2}}{C}$$

Billmeyer - or Solomon-Ciuta -

Results and Discussion

Values η_{red} and η_{inh} were calculated using measured efflux times and plotted versus C. As expected, these plots did show a curve at high and at low concentrations (Fig. 1). It was determined that a concentration range staring with 0.1 g of alginate dissolved in 100 mL of the 0.1 M NaCl solution gave the best straight lines (Fig 2.), which, when extrapolated to zero concentration (i.e. infinite dilution), gave [η].

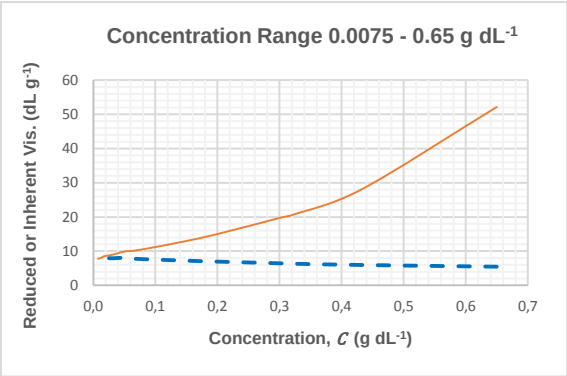

Figure 1. Conc. Range for Dilution method (Protanal LF)

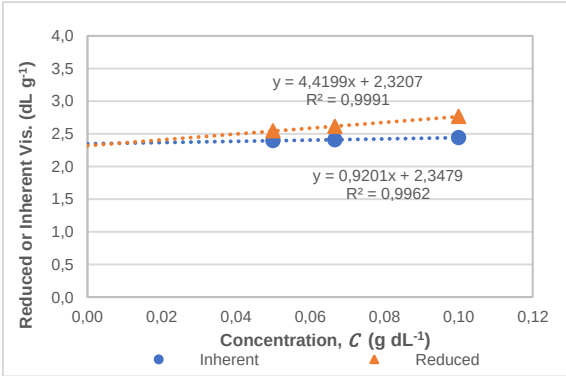

Figure 2. Intrinsic Viscosity for Sargassum Natans

Using a starting concentration of 0.1 g dL^{-1} (with subsequent dilutions to 0.0667 and 0.05 g dL^{-1}) [η] was determined for all four alginates. Additionally, [η] was determined using the two single-point methods. Using the experimentally determined [η] and values of M_w obtained independently for the four alginates, the constants K and a in the M-H-S equation were determined, with a correlation of 0.97.

These results are summarised in Table 1, which includes values of M_w calculated using the M-H-S equation, and determining the error between the calculated and experimentally found M_w.

Table 1. Intrinsic Viscosities and M-H-S Constants

Dilution method	Intinsic Viscosity	Mol Wt (GPC)	M-H-S K	M-H-S a	Mol Wt (cal.)	% Error
Sargassum Natans	2.59	344.6	1.44E-04	1.699	320.4	7.0%
Sigma-Aldrich	2.47	296.2			311.6	-5.2%
Manugel LBA	8.38	668.6			639.6	4.3%
Protanal LF	8.43	600.4			641.9	-6.9%
Billmeyer	**Intinsic Viscosity**	**Mol Wt (GPC)**	**M-H-S K**	**M-H-S a**	**Mol Wt (cal.)**	**% Error**
Sargassum Natans	2.59	344.6	1.74E-04	1.6682	317.8	7.8%
Sigma-Aldrich	2.54	296.2			314.3	-6.1%
Manugel LBA	8.53	668.6			649.3	2.9%
Protanal LF	8.16	600.4			632.1	-5.3%
Solomon-Ciuta	**Intinsic Viscosity**	**Mol Wt (GPC)**	**M-H-S K**	**M-H-S a**	**Mol Wt (cal.)**	**% Error**
Sargassum Natans	2.62	344.6	1.63E-04	1.680	317.8	7.8%
Sigma-Aldrich	2.57	296.2			314.3	-6.1%
Manugel LBA	8.69	668.6			649.2	2.9%
Protanal LF	8.30	600.4			632.1	-5.3%

Conclusions

- Using the Protanal LF, a concentration range of 0.10 to 0.05 dL g^{-1} was determined to be most suitable for carrying out multi-point analysis
- [η] values were determined to be between 2.47 and 8.69 dL g^{-1}
- The constants in the M-H-S Equation were determined to be K=1.44×10^{-4} dL g^{-1}, and a=1.70 for the multi-point method and for the single-point methods the average values were K=1.69×10^{-4} dL g^{-1} and a=1.67
- The [η] vs Mw data fitted the M-H-S equation with a correlation of 0.97.
- Once the M-H-S constants are known, the values of the M_w of the alginates may be determined via dilute solution viscometry rather than more detailed and expensive methods such as GPC.

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