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Various Models to Evaluate the Rheological Property of Hydrocolloid and Sweeteners Mixtures

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Abstract: Oscillatory rheometer was used to investigate the effects of some synthetic sweeteners (Aspartame, Acesulfame k, Cyclamate and Neotame) on rheological behavior of High Methoxylated Pectin (HMP) in dilute solutions. The concentration of these sweeteners were 0.1, 0.2% w/v for Aspartame, Acesulfame-k and Cyclamate and 0.001, 0.002% w/v for Neotame. We used various equations such as Huggins, Kraemer, Tanglerpaibul and Rao equations to assess the best model for determination intrinsic viscosity of HMP. The results showed that the values obtained for intrinsic viscosity were different by the equation used for estimation the intrinsic viscosity. We found $1-1/\eta_{rel}$ versus concentration plot as the best model. Addition of any of these four sweeteners had no significant effect on intrinsic viscosity of HMP in solutions.

Key words: High methoxylated pectin, intrinsic viscosity, sweetener, rheology

INTRODUCTION

Hydrocolloids are water-soluble, high molecular weight polysaccharides that serve a variety of functions in food systems, such as enhancing viscosity, creating gel-structures, formation of a film, control of crystallization, inhibition of syneresis, improving texture, encapsulation of flavors and lengthening the physical stability, etc. (Dickinson, 2003; Dziezak, 1991; Garti and Reichman, 1993; Glicksman, 1991).

Pectin is a polysaccharide consisting mostly of two moieties (Carpita and McCann, 2000). These are homogalacturonan, (1-4) linked, α -D-galacturonic acid and its methyl ester; and rhamnogalacturonan I, (1-2) repeating linked, α -L-rhamnose-(1-4) α -D-galacturonic acid disaccharide. Rhamnogalacturonan I contains arabinan, galactan and arabinogalactan side chains. These monosaccharide units comprise most of sugar units found in pectin.

The intrinsic viscosity, $[\eta]$, is not a very specific parameter and depends upon several factors (Bohdanecky and Kovar, 1982). It is dependent upon the hydrodynamic volume occupied per unit mass of the macromolecule; which consists of the intrinsic volume occupied by the polymer chain and its excluded free volume. It is also influenced by hydrodynamic properties which include a measure of the permeability of the polymer coil to solvent (if it is free draining, then $[\eta]$ is higher) and chain anisotropy. Deviations from spherical geometry add a frictional component to viscosity.

In another research, effects of some salts (NaCl, KCl and CaCl_2) on intrinsic viscosity of xanthan and locust bean gum interaction in dilute solution were investigated (Higiro *et al.*, 2006). Their results showed that a strong interaction occur between xanthan and LBG, even in dilute gum solution and these interactions are very strong with the 60% xanthan-40% LBG blend. But this interaction vanishes with the addition of salts. Also, addition of any of the three salts reduced significantly the intrinsic viscosity, with a pronounced effect from divalent ions, compared with monovalent ions.

Sweeteners are widely used low molecular weight additive; however, limited work has studied the influence of sweeteners upon the solution properties of hydrocolloids. For the case of guar and LBG, Elfak *et al.* (1977) found the intrinsic viscosity to decrease upon the addition of sucrose and other low molecular weight additives. Recently, in a similar but more extensive study by Launay *et al.* (1997), no change in intrinsic viscosity was measured for 0, 10 and 40% sucrose concentrations. There is not any study to investigation the effect of synthetic sweeteners on intrinsic viscosity of hydrocolloids.

The objective of this study was to explore the effect of some Synthetic sweeteners on the intrinsic viscosity of HMP in dilute solutions.

MATERIALS AND METHODS

Solution Preparation

HMP powder was purchased from Arman-Shayan Co., Iran. Acesulfame-k and Cyclamate were purchased from PT. Golden Sari (Jakarta Utara 14440, IND Onesia), Aspartame and Neotame were obtained from nutra sweet company, GC- 02032310 (USA).

Sweeteners/HMP solutions were prepared by dry mixing the appropriate amounts of each sweeteners and HMP. Cold de-ionised water was then added and the solutions were heated at 60° C for 15 min whilst stirring with a magnetic flea. Molecular weight analyses (Russell, 1997 unpublished data) showed that the polymer did not degrade at these temperatures unless excessive mechanical stirring was used. Dilute HMP solutions were prepared (0.005, 0.01, 0.02, 0.03, 0.04 and 0.05 g dL⁻¹) in the ranges of sweeteners concentrations (0.1, 0.2% w/v for Aspartame, Acesulfame and Cyclamate and 0.001, 0.002% w/v for Neotame). The control samples were HMP solutions without any sweetener.

Viscosity Measurement

The viscosity of gum solutions were measured as a function of oscillating shear rate by using an oscillatory rheometer (MCR 300, PAAR Co. Germany), which is used to measure the oscillatory viscosity of fluids.

The viscosity was determined at a frequency of 2 Hz (Thurston, 1996) within a shear-rate range of 0.8-20 sec⁻¹. Morris and Taylor (1982) reported that oral perception of solution viscosity correlated well with viscosity measurements at 10 sec⁻¹. Thus, all viscosity measurements were statistically assessed at 10 sec⁻¹. Rheological measurements were carried out at 20°C by using a temperature-controlled circulating water bath. The analyzer was calibrated with de ionized distilled water at 20°C, followed by the verification procedure to further ensure that the rheometer was operating at optimum conditions.

Statistical Analysis

A two-way factorial design was used to generate the best-fitting intrinsic viscosity model. The sweeteners (Aspartame, Acesulfame, Cyclamate and Neotame) at two concentrations (0.1 and 0.2% w/v for Aspartame, Acesulfame and Cyclamate and 0.001, 0.002% w/v for Neotame) were compared for the intrinsic viscosity, in a factorial design. In each instance, three replications were made. The analysis of variance and means comparison were conducted by the general linear models procedure (Proc GLM), with Statistical Analysis System software (version 9.1, SAS Institute, Inc., Cary, NC). Comparisons among treatments were analyzed by using Fisher's Least Significant Difference (LSD), with a significance level at p<0.05.

Intrinsic Viscosity Determination

The intrinsic viscosity [η] was measured according to the method used by Higiroy *et al.* (2006). In their research, they used five ways to determine the intrinsic viscosity following:

Huggins (1942) equation:

$$\frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2 c \quad (1)$$

Kraemer (1938) equation:

$$\frac{\ln \eta_{rel}}{C} = [\eta] + k''[\eta]^2 \quad (2)$$

Tanglertpaibul and Rao (1987) equation:

$$\eta_{rel} = 1 + [\eta]C \quad (3)$$

Higiro *et al.* (2006) have proposed two other ways to obtain intrinsic viscosity from the Eq. 3

$$\eta_{rel} = e^{[\eta]C} \quad (4)$$

According to that, the intrinsic viscosity is the slope obtained by plotting $\ln \eta_{rel}$ vs. C

$$\eta_{rel} = \frac{1}{1 - [\eta]c} \quad (5)$$

According to that, the intrinsic viscosity is the slope obtained by plotting $1 - \frac{1}{\eta_{rel}}$ vs. C

RESULTS AND DISCUSSION

Intrinsic Viscosity

In general, an increase in specific viscosity was observed as the concentration decreased Fig. 1. The intrinsic viscosity determination by extrapolating to zero concentrations therefore failed to

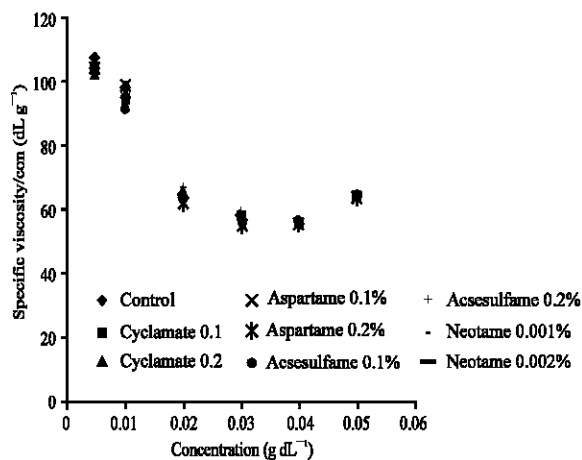


Fig. 1: Huggins plot (specific viscosity/concentration vs. concentration) for HMP with addition of sweeteners

generate the intrinsic viscosity for HMP and the data did not fit with the linear regression model. Lapasin and Prici (1995) reported that neutral polysaccharides, exhibited linear plots of lower slope, whereas ionic polysaccharides (i.e., HMP) displayed a sharp increase of the slope, possibly due to expanded coil dimensions and electrostatic repulsion between chain segments.

We observed the same results for HMP. Figure 1 displays increasing of specific viscosity/concentration as concentration decreases below 0.03.

Lai *et al.* (2000) reported similar results when determining the intrinsic viscosity of Hsian-tso leaf gum in different salt solutions. Other works showed the same results for mixture of gum and salts (Pals and Hermans, 1952; Higiroy *et al.*, 2006).

Present results showed that effects of addition of any of the four sweeteners depend on types and concentrations of sweeteners and the equation that is used. Different equations, give different intrinsic viscosities.

From Eq. 1, the Huggins constant k' theoretically should lie between 0.3 and 0.8 and values larger than 1 imply polymer-polymer aggregation (Morris, 1995b). We found the k values in this range (data not shown). The sum of the Huggins constant k and Kraemer constant k' should equal $0.5 \pm 10\%$ (Fig. 2 and larger or smaller values are attributed to molecule association (Morris *et al.*, 1981; Higiroy *et al.*, 2006). Values from this study fall within this range, meaning molecular association was absent.

The non-linear relationship between η_{sp}/C and gum concentration was observed at low HMP concentrations, thus making impossible the determination of the intrinsic viscosity by extrapolation of experimental data; this prompted the use of slope models (Chou and Kokini, 1987; Tanglertpaibul and Rao, 1987) to determine the intrinsic viscosity by plotting relative viscosity vs. C Eq. 3 and $\ln \eta_{rel}$ vs. C Eq. 4. Straight-line relationships with large linear regression coefficients was obtained (Fig. 3 and 4). McMillan (1974) reported that methods of determination of intrinsic viscosity based on slopes of plots had larger correlation coefficients and smaller standard errors than did those based on intercepts of plots.

Intrinsic viscosity values calculated by using Eq. 3 were larger and significantly different from those obtained by using Eq. 4 and 5 for all sweeteners and sweetener concentrations. We saw the same results. Tanglertpaibul and Rao (1987) successfully implemented the model from Eq. 3 in the intrinsic viscosity determination of tomato serum. The results reported higher correlation coefficients and fewer errors. Significant differences between guar gum were detected with Eq. 3, whereas these differences were few with Eq. 4 and 5. We used Eq. 3 as the best model for intrinsic viscosity

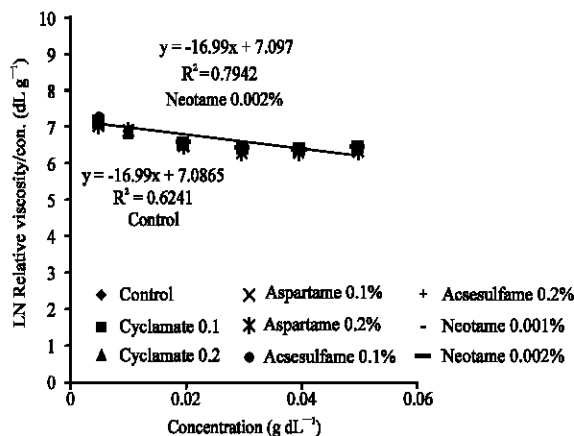


Fig. 2: Kraemer plot ($\ln \eta_{rel}$ relative viscosity/concentration vs. concentration) for HMP with addition of sweeteners

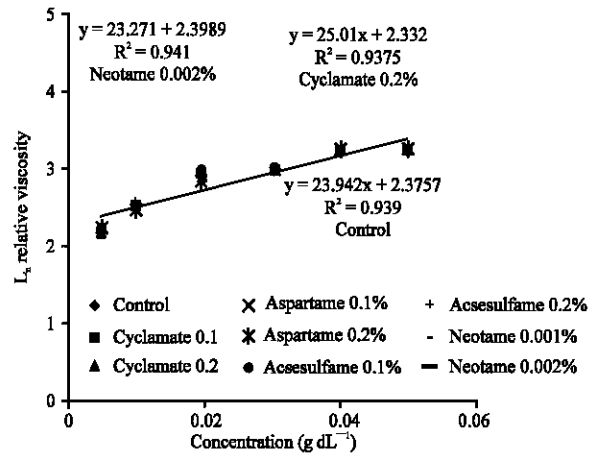


Fig. 3: L_n Relative viscosity for HMP as a function of gum concentration with addition of sweeteners

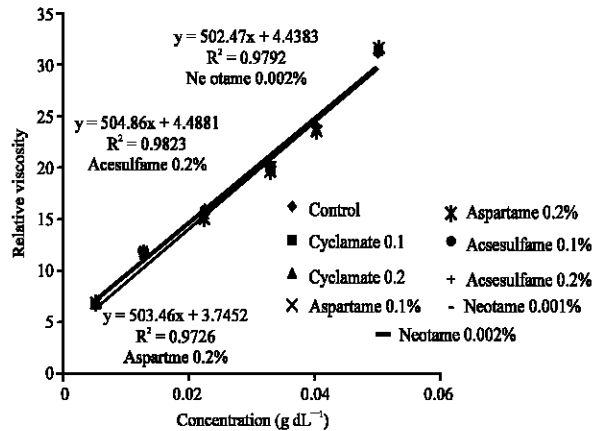


Fig. 4: Relative viscosity for HMP as a function of gum concentration with addition of sweeteners

determination because it showed a better linear fit, with higher correlation (R^2) for gum, sweeteners and sweetener concentrations (Fig. 5). Furthermore, the results were similar to other findings (Tanglertpaibul and Rao, 1987). Richardson *et al.* (1998) studied the effect of sucrose on dilution solution properties of galactomannans. Their results showed that addition of sucrose at low concentrations (0-10% w/w) decrease the intrinsic viscosity (because of decreasing the solvent quality) and these results can complimented the Huggins model. Sucrose influence the intrinsic viscosity by changing structure of the hydrocolloid (coil expansion) and so rheological behavior.

Present results showed that the values obtained for intrinsic viscosity were different by the equation used for estimation the intrinsic viscosity. We found relative viscosity versus concentration plot as the best model. Addition of any of these four sweeteners had no significant effect on intrinsic viscosity of HMP gum solutions, indicated these synthetic sweeteners had any affects on solvent quality and hydrodynamic volume of HMP.

The representative comparison of the different models used to estimate the intrinsic viscosity is shown for HMP (Table 1).

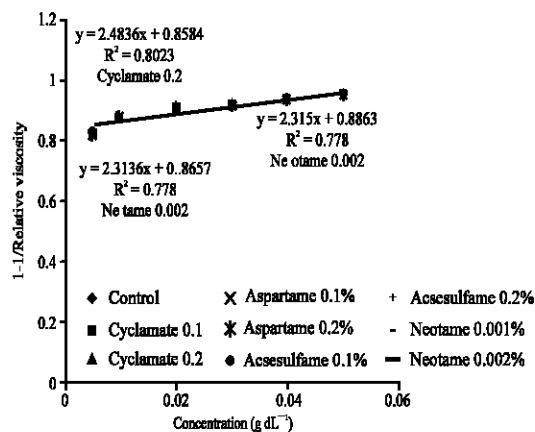


Fig. 5: Plot of $(1-1/\text{Relative viscosity})$ as a function of gum concentration for HMP with addition of sweeteners

Table 1: Intrinsic viscosity values (dL g^{-1}) obtained for HMP using different models

Sweetener	Sweetener con. (%)	1	2	3	4	5
Aspartame	0	-	-	509.08 ± 6.0^a	23.94 ± 2.3^b	2.31 ± 0.2^c
	0.1	-	-	503.13 ± 4.2^a	23.96 ± 2.5^b	2.30 ± 0.2^c
	0.2	-	-	503.46 ± 4.8^a	25.06 ± 2.1^b	2.39 ± 0.1^c
Acesulfame-k	0	-	-	509.08 ± 6.0^a	23.94 ± 2.3^b	2.31 ± 0.2^c
	0.1	-	-	509.54 ± 6.3^a	25.22 ± 2.4^b	2.40 ± 0.2^c
	0.2	-	-	504.86 ± 5.4^a	25.06 ± 2.8^b	2.31 ± 0.1^c
Cyclamate	0	-	-	509.08 ± 6.0^a	23.94 ± 2.3^b	2.31 ± 0.2^c
	0.1	-	-	503.81 ± 5.3^a	24.48 ± 2.7^b	2.41 ± 0.1^c
	0.2	-	-	507.42 ± 6.0^a	25.01 ± 2.8^b	2.48 ± 0.2^c
Neotame	0	-	-	509.08 ± 6.0^a	23.94 ± 2.3^b	2.31 ± 0.2^c
	0.001	-	-	507.93 ± 6.9^a	24.67 ± 2.8^b	2.32 ± 0.1^c
	0.002	-	-	502.47 ± 4.1^a	23.27 ± 3.1^b	2.31 ± 0.1^c

Results are expressed as means \pm SD for three replications; A-B: Means followed by the same letter(s) in the same row are not significantly different ($p < 0.05$). a-b : Means followed by the same letters in the same column are not significantly different ($p < 0.05$). -: Not estimated by Huggins and Kraemer equations

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CONCLUSIONS

The Huggins Eq. 1, Kraemer (Eq. 2) and $1-1/\eta_{\text{rel}}$ vs. C (Eq. 5) plots do not provide a better fit for Aspartame, Acesulfame, Cyclamate and Neotame in regular concentrations. Using any of equations result in different values for intrinsic viscosity. To determine the intrinsic viscosity by plotting relative viscosity vs. C (Eq. 3), $\ln \eta_{\text{rel}}$ vs. C (Eq. 4), Straight-line relationships with large linear regression coefficients obtain for HMP but relative viscosity vs. C versus concentration plot was selected as best model because of its higher linear coefficient. By using these appropriate equations, there are not any significant difference among these sweeteners, indicate that these synthetic sweeteners had any affects on solvent quality and hydrodynamic volume of HMP may be due to their low concentrations. It is possible that when their concentrations increased, their effects become significant.

REFERENCES

- Bohdanecky, M. and J. Kovar, 1982. The Viscosity of Polymer Solutions of Finite Concentration. In: Viscosity of Polymer Solutions. Jenkins, A.D. (Ed.), Polymer Science Library 2, Amsterdam: Elsevier, pp: 166-220.
- Carpita, N. and M.C. McCann, 2000. The Cell Wall. In: Biochemistry and Molecular Biology of Plants. Buchanan, B. (Ed.), Rockville, MD: Am. Soc. Plant Physiologists, pp: 52-108.
- Chou, T.D. and J.L. Kokini, 1987. Rheological properties and conformation of tomato paste pectins, citrus and apple pectins. *J. Food Sci.*, 52: 1658-1664.
- Dickinson, E., 2003. Hydrocolloids at interfaces and the influence on the properties of dispersed systems. *Food Hydrocolloids*, 17: 25-39.
- Dziezak, J.D., 1991. A focus on gums. *Food Technol.*, 45: 116-132.
- Elfak, A.M., G. Pass, G.O. Philips and R.G. Morley, 1977. The viscosity of dilute solutions of guar gum and locust bean gum with and without added sugar. *J. Sci. Food. Agric.*, 28, 895-899.
- Garti, N. and D. Reichman, 1993. Hydrocolloids as food emulsifiers and stabilizers. *Food Struct.*, 12: 411-426.
- Glicksman, M., 1991. Hydrocolloids and search for the oily grail. *Food Technol.*, 94: 96-103.
- Heitmann, D.I.T. and A. Mersmann, 1995. Determination of the intrinsic viscosity of native potato starch. *Starch/Stärke*, 47: 426-429.
- Higiro, J., T.J. Herald, S. Alavi and S. Bean, 2006. Rheological study of xanthan and locust bean gum interaction in dilute solution: Effect of salts. *Food Res. Int.* (In Press).
- Huggins, M.L., 1942. The viscosity of dilute solutions of long-chain molecules. IV. Dependence on concentration. *J. Am. Chem. Soc.*, 64: 2716-2718.
- Kraemer, E.O., 1938. Molecular weights of celluloses and cellulose derivatives. *Indus. Eng. Chem.*, 30: 1200-1203.
- Lai, L.S., J. Tung and P.S. Lin, 2000. Solution of hsian-tsoa (*Mesona procumbens* Hemsl) leaf gum. *Food Hydrocolloids*, 14: 287-294.
- Lai, L.S. and H.F. Chiang, 2002. Rheology of decolorized hsian-tsoa leaf gum in the dilute domain. *Food Hydrocolloids*, 16: 427-440.
- Lapasin, R. and S. Priel, 1995. Rheology of polysaccharide systems.
- Launay, B., G. Cuvelier and S. Martínez-Reyes, 1997. Viscosity of locust bean, guar and xanthan gum solutions in the Newtonian domain: A critical examination of the $\log(\eta_{sp})/\log C(\eta)$ master curves. *Carbohydrate Polymers*, 34: 385-395.
- McMillan, D.E., 1974. A comparison of five methods for obtaining the intrinsic viscosity of bovine serum albumin. *Biopolymers*, 13: 1367-1371.
- Morris, A.M., E.R. Cutler, A.N. Ross-Murphy, S.B. and Rees, D. A. 1981. Concentration and shear rate dependence of viscosity in random coil polysaccharide solutions. *Carbohydrate Polymers*, 1: 5-21.
- Morris, E.R. and L.J. Taylor, 1982. Oral perception of fluid viscosity. *Progress Food Nutr. Sci.*, 6: 285-296.
- Morris, E.R., 1995. Polysaccharide Rheology and in-Mouth Perception. In: Rheology of Industrial Polysaccharides: Theory and Application. Lapasin, R. and S. Priel (Eds.), Glasgow: Blackie Academic and Professional, pp: 250-494.
- Pals, D.T. and J.J. Hermans, 1952. Sodium salts of pectin and carboxymethyl cellulose in aqueous sodium chloride. *Recueil des Travaux Chimiques des Pays Bas*, 71: 433-443.
- Richardson, P.H., J. Willmer and T.J. Foster, 1998. Dilute solution properties of guar and locust bean gum in sucrose solutions. *Food Hydrocolloids*, 12: 339-348.
- Tanglertpaibul, T. and M.A. Rao, 1987. Intrinsic viscosity of tomato serum as affected by methods of determination and methods of processing concentrates. *J. Food Sci.*, 52, 1642-1688.
- Thurston, G., 1996. Viscoelastic Properties of Blood and Blood Analogs. In: Advances in Haemodynamics and Haemorheology. How, T. (Ed.), New York: JAI Press, pp: 1-34.