

Flow properties of sugar beet pulp cellulose and intrinsic viscosity–molecular weight relationship

Hasan Toğrul, Nurhan Arslan*

Faculty of Engineering, Department of Chemical Engineering, Firat University, 23279 Elazığ, Turkey

Received 27 November 2002; revised 2 May 2003; accepted 6 May 2003

Abstract

Cellulose was extracted with 5, 10, 15% NaOH at 25, 35, 45 °C for 10, 16, 22 h from defatted, protein, pectin and hemicellulose free, delignified sugar beet pulp. Extraction with 10% NaOH at 35 °C for 22 h gave the highest yield of the removal of substances with the exception of cellulose. The effects of temperature and concentration on the viscosity of sugar beet pulp cellulose solutions were examined at different temperatures and concentration levels. Twenty-eight different model equations that describe the combined effects of temperature and concentration on the viscosity were derived. Theoretical models describing the temperature and concentration dependence of viscosity were fitted to the experimental data and the model parameters in equations were determined by multiple regression analysis of the experimental data in the temperature range 10–60 °C and in the concentration range 0.5–10 kg/m³. The viscosity of cellulose from sugar beet pulp can be predicted by the single equation: $\ln \eta = -2.8C^{0.0186} + 1031C^{0.025}/T + 2654 \exp(0.1896C)/T^2$.

The average molecular weight was measured by light scattering technique. Intrinsic viscosities and molecular weights of cellulose obtained at different extraction conditions ranged between 0.347–0.0836 m³/kg and 303,200–893,500 kg/kg mol, respectively. The molecular weight dependence of the intrinsic viscosity of the sugar beet pulp cellulose solutions was expressed by Mark-Houwink-Sakurada equation. The intrinsic viscosity–molecular weight relationship was found as $\eta_i = 2.313 \times 10^{-6} (M_{w,ave})^{0.7665}$.

© 2003 Elsevier Ltd. All rights reserved.

Keywords: Sugar beet pulp; Cellulose; Temperature and concentration dependence; Intrinsic viscosity; Molecular weight

1. Introduction

Cellulose is a polydisperse polymer of high molecular weight comprised of long chains of D-glucose units joined together by β -1,4-glucosidic bonds (Kirk & Othmer, 1967). Cellulose is plant cell wall component and is widely distributed in plant foods (Wen, Chang, Brown, & Gallaher, 1988). Sugar beet pulp, a lignocellulosic by-product of the sugar industry, is a well-known potential source of cellulose as the lignocellulosic fraction of dried sugar beet pulp contains 22–30% cellulose (Coughlan, Mehra, Considine, O'Rourke, & Puls, 1985). The cellulose obtained from sugar beet pulp have a strong potential for a number of applications in which rheology is important (Sun & Hughes, 1998).

Viscosity is a measure of molecular weight and the higher the molecular weight, the higher is its viscosity.

The viscosity depends not only on the molecular weight but also on concentration, temperature (Kar & Arslan, 1999). Therefore, viscosity must be correlated with both molecular weight and concentration, temperature. The molecular weight of polymers have been determined using high performance size exclusion chromatography, gel permeation chromatography, differential refractometer and low-angle laser light scattering detection (Hirrien, Desbrieres, & Rinaudo, 1996; Kennedy, Rivera, Lloyd, Warner, & Silva, 1995; Pang & Rudin, 1992; Sun, Fang, Tomkinson, Geng, & Liu, 2001). The molecular weight of sugar beet pulp cellulose can be determined with the knowledge of the intrinsic viscosity. Information on the intrinsic viscosity of cellulose solutions has been reported (Johnston & Sourirajan, 1973). However, at present no attempt was made to determine the molecular weight of sugar beet pulp cellulose using light scattering technique and to show the intrinsic viscosity–molecular weight relationship.

Knowledge on the effect of temperature and concentration on viscosity is essential for the design and evaluation

* Corresponding author. Fax: +90-424-2415526.
E-mail address: narslan2@firat.edu.tr (N. Arslan).

of food processing equipment such as piping, evaporators and heat exchangers. Study of the flow properties is of particular interest in engineering calculations related to the processing and handling of sugar beet pulp cellulose. With regard to engineering calculations, knowledge of the applicable flow models is important for design of flow systems (Rao & Anantheswaran, 1982).

The aims of the present study were to extract the cellulose from sugar beet pulp, to develop theoretical models which describing the temperature and concentration dependence of the viscosity of sugar beet pulp cellulose solutions, and to find intrinsic viscosity–molecular weight relationship of sugar beet pulp cellulose solutions.

2. Materials and methods

2.1. Chemical analysis of sugar beet pulp

Moisture, protein and ash were determined by AOAC methods (AOAC, 1984). Crude fat was determined gravimetrically after extraction with petroleum ether. Polysaccharide was determined by difference. All results were expressed on a dry weight basis determined by drying samples at 105 °C for 12 h. All experiments in this study were conducted in duplicate.

2.2. Extraction of cellulose from sugar beet pulp

Sugar beet pulp obtained from the Elaziğ (Turkey) Sugar Factory was sun-dried and ground in a hammer mill to pass a 50-mesh size screen. The ground pulp was heated to 97 °C in a water bath for about 10 min to inactivate pectic enzymes. Then, it was washed with water, filtered through a suction filter, dried at 50 °C and sieved. A 50-mesh fraction was used in experiments. The dried and ground sugar beet pulp (7 g) was defatted by extraction with chloroform: methanol (2:1, v/v) in soxhlet for 6 h. The defatted sugar beet pulp was mixed with 350 ml of 0.1 M Na₃PO₄ to bring to pH 7.5. Proteolysis was performed by the addition of protease (35 mg). After incubation overnight at 37 °C, the sample was filtered. The deproteinated sugar beet pulp was mixed with 700 ml of 0.25% ammonium oxalate (w/v) (pH 3.5). The mixture was shaken at 75 °C in water bath for 60 min and filtered. NaOH of 5, 10, 15% (1 g residue/100 ml extractant) was added the depectinated sugar beet pulp. The mixture was shaken at 25, 35, 45 °C in water bath for 10, 16, 22 h, filtered and washed distilled water to remove the base. The hemicellulose-free sugar beet pulp was mixed with 100 ml of distilled water, 5 ml of 10% acetic acid and 2 g NaCl. The mixture was shaken at 75 °C in water bath for 60 min and filtered. The residue was washed with distilled water and ethanol to remove acid, and then dried at 50 °C in an oven for 16 h. The scheme of extraction stages for cellulose from sugar beet pulp is shown in Fig. 1.

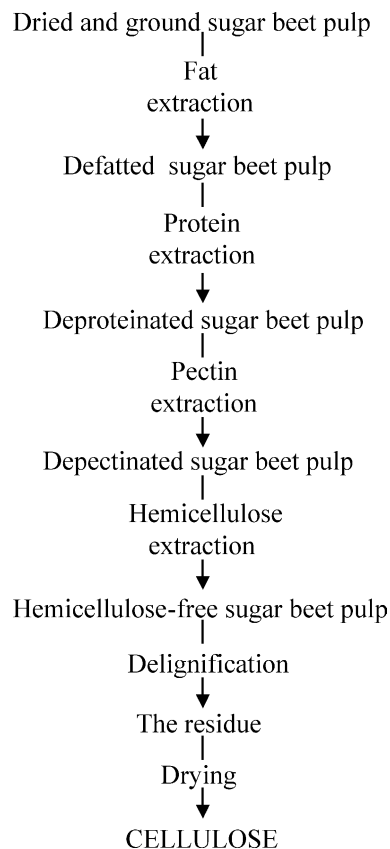


Fig. 1. Scheme for extraction of cellulose from sugar beet pulp.

2.3. Viscosity measurements

The strong mineral acids dissolve cellulose in certain concentration ranges. Dissolution of cellulose may be presumed to be due to the formation of the $-\text{OH}_2^+$ ion attached to the cellulose (Ott, 1946). Therefore, cellulose solutions were prepared by dissolving the cellulose in 37% HCl. Solutions were stirred to completely solubilize the cellulose. Solutions with concentration of 0.5, 0.75, 1.0, 1.5, 2.5, 5, 7.5 and 10 kg/m³ were prepared, filtered through filter and the viscosities of cellulose solutions in different concentrations were determined at 10 °C intervals from 10 to 60 °C using an Ubbelohde type capillary viscosimeter (capillary no: II, ID: 1.13 mm) immersed in a thermostated water bath. The viscosity measurements did not changed significantly as a function of time. Flow times were recorded with a stopwatch with reproducibility ± 0.2 s. Densities of solutions were measured using a 25 ml Gay-Lussac pycnometer. The relative viscosity can be used to describe the viscosity of solutions and is defined as (Chamberlain & Rao, 2000)

$$\eta_r = \eta/\eta_s \quad (1)$$

where η_r is the relative viscosity, η is the viscosity cellulose solution (Pa s), η_s is the viscosity of solvent (1.972 mPa s).

The relative viscosities were calculated for 0.5, 0.75, 1.0, 1.5 and 2.5 kg/m³ concentrations. Relative viscosity values

were converted to specific viscosities (η_{sp}) using the following equation (Ng, Tam, & Jenkins, 1999)

$$\eta_{sp} = \eta_r - 1 \quad (2)$$

When the solution concentration approaches zero, the reduced viscosity (η_{sp}/C) approach the intrinsic viscosity. The reduced viscosity was plotted against concentration and the intrinsic viscosity was obtained by extrapolation of the reduced viscosity to zero polymer concentration using the Staudinger equation (Pagan & Ibarz, 1999)

$$\eta_i = \lim_{C \rightarrow 0} (\eta_{sp}/C) \quad (3)$$

where C is the concentration of cellulose solution (kg/m^3), η_{sp} is the specific viscosity, η_i is the reduced viscosity (m^3/kg).

2.4. Determination of molecular weight

The refractive indexes of cellulose solutions were measured by a refractometer using a mono-chromatic source of sodium vapour lamp. The intensity of light scattered through cellulose solutions was measured as the percentage of light transmitted through cellulose solutions, as compared to that through 37% HCl by spectronic 20 spectrophotometer. The experimental measurements were made at five different concentrations (0.5, 0.75, 1.0, 1.5 and 2.5 kg/m^3) at 20 °C.

The average molecular weight of the cellulose was calculated by following equation (Allock & Lampe 1981; Rao, 1993)

$$1/M_{w,ave} = \lim_{C \rightarrow 0} (HC/\tau) \quad (4)$$

where $M_{w,ave}$ is the average molecular weight ($\text{kg}/\text{kg mol}$), τ is the turbidity of solution (m^{-1}).

H is given (Allock & Lampe, 1981) by

$$H = (32\pi^3 n_0^2 / 3\lambda^4 N_A) ((n - n_0)/C)^2 \quad (5)$$

where n_0 is the refractive index of the solvent (37% HCl, 1.4062), n is the refractive index of the solution, λ is the wave length of light ($0.5893 \times 10^{-6} \text{ m}$), N_A is the Avogadro number (6.023×10^{23}).

The turbidity of the solutions was measured as the decrease in the intensity of a beam of light because of scattering. The decrease depends on the length of the light path through the system (Allock & Lampe, 1981) and, by analogy to the Lambert law it is possible to write

$$I/I_0 = e^{-\tau l} \quad (6)$$

where I/I_0 is the fraction of light transmitted through 1 cm length of solution, l is the length of the light path in the solution (m).

The fraction of light scattered is generally very small and it is a good approximation to express the exponential in

the above equation (Allock & Lampe, 1981) as

$$e^{-\tau l} \cong 1 - \tau l \quad (7)$$

$$\tau l = 1 - e^{-\tau l} = 1 - (I/I_0) \quad (8)$$

$M_{w,ave}$ was measured by plotting HC/τ versus C and interpolating to zero concentration and noting the value of intercept.

3. Results and discussion

The dried sugar beet pulp contained 3.72% ash, 8.92% crude protein, 1.1% crude fat on a dry weight basis. By difference, polysaccharide content was calculated as 86.26%. The effect of alkali concentration, time and temperature on cellulose yield (%dry weight of sugar beet pulp) is shown in Table 1.

As seen from Table 1, the yield of cellulose ranged between 17.00 and 32.01%. The yield of cellulose decreased with increasing time and alkali concentration at a given temperature. The yield of cellulose decreased with temperature for extraction time of 10 h at all alkali concentrations while the harmonious trends were not observed for extraction times of 16 and 22 h. The substances of 67.99, 72.89 and 73.36% with the exception of cellulose were removed for extraction times of 10, 16 and 22 h in experiments performed at 25 °C with alkali concentration of 5% (the removal percentage of substances with the exception of cellulose: $100 - \text{cellulose yield}\%$). The condition that the removal yields of substances with the exception of cellulose was the highest were determined as optimum condition since the substances with the exception of cellulose were well removed in low cellulose yield. Since a increase of 5% in alkali concentration at 35 °C for 22 h causes only a improvement of 1.1%, the optimum condition was selected as 35 °C, 10% NaOH and 22 h instead of 35 °C, 15% NaOH and 22 h. Those choose was more economic because of extra alkali consumption. Sun and Hughes (1998) extracted the cellulose with 7.5%

Table 1
Yield of cellulose extracted from sugar beet pulp

T (°C)	NaOH%	Time (h)		
		10	16	22
25	5	32.01	27.11	26.64
	10	30.45	23.44	21.42
	15	30.27	21.68	18.32
35	5	29.87	26.93	23.02
	10	29.40	25.32	17.20
	15	26.78	25.25	17.00
45	5	28.61	25.47	23.82
	10	26.71	22.95	22.80
	15	26.40	22.90	19.50

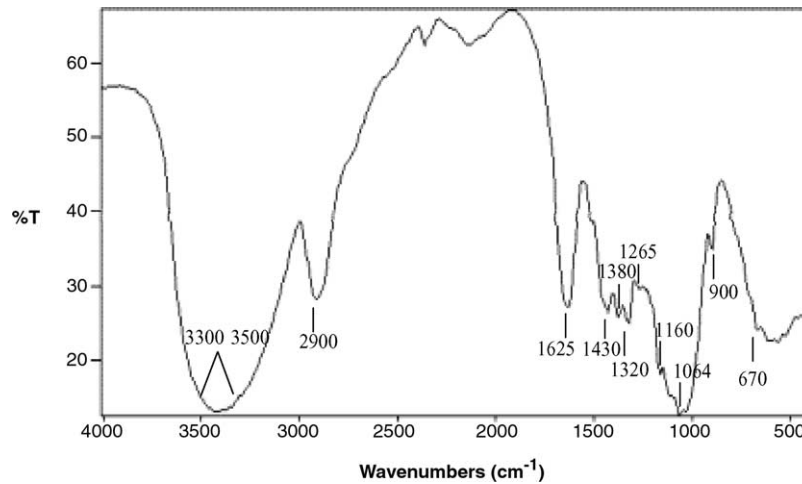


Fig. 2. The infrared spectrum of cellulose from sugar beet pulp.

NaOH at 15 °C for 16 h from sugar beet pulp, and found that the yield of cellulose was 14.88%.

The IR-spectrum was recorded (ATI UNICAM 1000 MATTSON Spectrometer) to find out the characteristic groups in cellulose from sugar beet pulp at the optimum conditions (Fig. 2).

The IR-spectrum gives very typical peaks for a number of special groups. As shown in Fig. 2, the band at 670 cm⁻¹ is OH out-of-plane bending band. An absorption band at 900 cm⁻¹ indicates the β-glycosidic linkages. The prominent band at 1064 cm⁻¹ represents ring vibration and C–OH bending. The band at 1160 cm⁻¹ is attributable to the C–O and C–O–C stretching. There are C–H bending vibration bands at 1265 and 1380 cm⁻¹. The band at 1320 cm⁻¹ represents OH in plane bending or CH bending. The peak at 1430 cm⁻¹ shows CH₂ bending. The characteristic peak at 1625 cm⁻¹ is –O– tensile vibration band neighbouring to H group. The peak at 2900 cm⁻¹ is tertiary C–H asymmetric and symmetric tensile vibration band. The ample peak at 3300–3500 cm⁻¹ shows OH stretching bands of H bonds.

3.1. The combined effect of temperature and concentration on viscosity

It has been assumed that the cellulose solutions studied were Newtonian since diluted organic solutions are generally Newtonian in character (Kirk & Othmer, 1970).

Fig. 3 shows the effect temperature and concentration on the viscosity of cellulose solutions (0.5, 0.75, 1.0, 2.5, 5.0, 7.5 and 10 kg/m³) prepared from cellulose obtained at the optimum reaction conditions.

As seen from Fig. 3, at higher temperature, viscosity decreases and at higher concentration viscosity increases. As expected, an increase in temperature decreased the viscosity and this inverse relationship has been likened to the incidence of a freer molecule to molecule interaction

at elevated temperatures. Since viscosity is an indication of the resistance to flow (Howard, 1991) such a freer interaction is expected to minimize the resistance. When the solid concentration increases, the viscosity increases because of the increase in hydrogen bonding with hydroxyl groups and the distortion in the velocity pattern of the liquid by hydrated molecules of solute. The intermolecular distances that is also a factor that affects the viscosity is inversely proportional to it due to changing temperature.

The effect of temperature on the viscosity of fluids can be expressed by Arrhenius and Andrade equations (Abramovic & Klofutar, 1998; Constella, Lozano, & Crapiste, 1989; Rao, Cooley, & Vitali, 1984)

$$\eta = \eta_0 \exp(E_a/RT) \quad (9)$$

$$\ln \eta = A + B/T + C/T^2 \quad (10)$$

$$\ln \eta = A + B/T + CT \quad (11)$$

$$\log \eta = A/T - B \quad (12)$$

$$\eta = A - B \log T \quad (13)$$

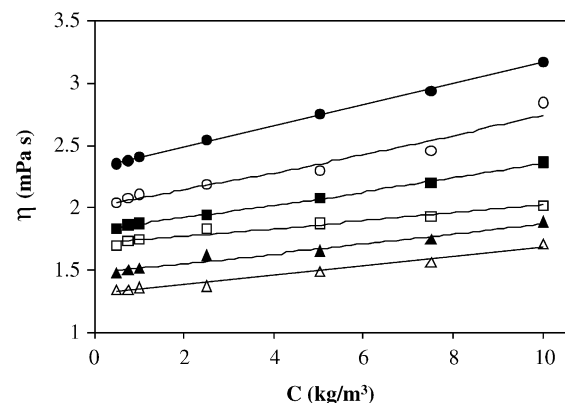


Fig. 3. Change in the viscosity of cellulose solutions with concentration at different temperatures (temperature (°C): ●, 10; ○, 20; ■, 30; □, 40; ▲, 50; △, 60).

Table 2

Values of parameters of the theoretical models

Model 1	Model 2	Model 3
$\eta = K_3 C^{A_3} \exp(K_5 C^{A_5}/RT)$ $K_3 = 0.076731 \text{ mPa s (kg/m}^3)^{-A_3}$ $A_3 = -0.355620 (-)$ $K_5 = 8057.135 \text{ (J/mol) (kg/m}^3)^{-A_5}$ $A_5 = 0.122098 (-)$ RMSE = 0.021184; MBE = 0.000231 MPE = -0.13058; $\chi^2 = 0.003358$ EF = 0.9846; $r = 0.9923$	$\eta = K_3 C^{A_3} \exp(K_6 \exp(A_6 C)/RT)$ $K_3 = 0.052676 \text{ mPa s (kg/m}^3)^{-A_3}$ $A_3 = -0.001369 (-)$ $K_6 = 8941.115 \text{ (J/mol)}$ $A_6 = 0.007371 \text{ (kg/m}^3)^{-1}$ RMSE = 0.005546; MBE = -0.00037 MPE = -0.02405; $\chi^2 = 0.003358$ EF = 0.9909; $r = 0.9954$	$\eta = K_4 \exp(A_4 C) \exp(K_5 C^{A_5}/RT)$ $K_4 = 0.050256 \text{ mPa s}$ $A_4 = 0.024691 \text{ (kg/m}^3)^{-1}$ $K_5 = 9063.522 \text{ (J/mol) (kg/m}^3)^{-A_5}$ $A_5 = 0.002046 (-)$ RMSE = 0.004297; MBE = 0.001012 MPE = -0.09872; $\chi^2 = 0.002546$ EF = 0.98841; $r = 0.9942$
Model 4	Model 5	Model 6
$\eta = K_4 \exp(A_4 C) \exp(K_6 \exp(A_6 C)/R)$ $K_4 = 0.071445 \text{ mPa s}$ $A_4 = -0.066924 \text{ (kg/m}^3)^{-1}$ $K_6 = 8215.583 \text{ (J/mol)}$ $A_6 = 0.025016 \text{ (kg/m}^3)^{-1}$ RMSE = 0.009563; MBE = -0.0003 MPE = 0.005046; $\chi^2 = 0.00205$ EF = 0.990654; $r = 0.9953$	$\ln \eta = K_7 C^{A_7} + K_9 C^{A_9}/T + K_{11} C^{A_{11}}/T^2$ $K_7 = -1.11839 \text{ (kg/m}^3)^{-A_7}$ $A_7 = -0.025601 (-)$ $K_9 = 0.17756 \text{ K (kg/m}^3)^{-A_9}$ $A_9 = 2.374449 (-)$ $K_{11} = 160,866 \text{ K}^2 \text{ (kg/m}^3)^{-A_{11}}$ $A_{11} = -0.039167 (-)$; RMSE = 0.002927 MBE = -0.00026; MPE = -0.01859 $\chi^2 = 0.001637$; EF = 0.992933; $r = 0.9961$	$\ln \eta = K_7 C^{A_7} + K_9 C^{A_9}/T + K_{12} \exp(A_{12} C)/T^2$ $K_7 = -2.799607 \text{ (kg/m}^3)^{-A_7}$ $A_7 = 0.018556 (-)$ $K_9 = 1031.119 \text{ K (kg/m}^3)^{-A_9}$ $A_9 = 0.025036 (-)$ $K_{12} = 2654.188 \text{ K}^2$ $A_{12} = 0.189627 \text{ (kg/m}^3)^{-1}$ RMSE = 0.005531; MBE = -0.00036 MPE = -0.01709; $\chi^2 = 0.001597$ EF = 0.993104; $r = 0.9964$
Model 7	Model 8	Model 9
$\ln \eta = K_7 C^{A_7} + K_{10} \exp(A_{10} C)/T + K_{11} C^{A_{11}}/T^2$ $K_7 = -2.80378 \text{ (kg/m}^3)^{-A_7}$ $A_7 = -0.016420 (-)$ $K_{10} = 1047.998 \text{ K}$ $A_{10} = -0.010528 \text{ (kg/m}^3)^{-1}$ $K_{11} = 1902.784 \text{ K}^2 \text{ (kg/m}^3)^{-A_{11}}$ $A_{11} = 1.346493 (-)$ RMSE = 0.006452; MBE = -0.00036 MPE = -0.01753; $\chi^2 = 0.001633$ EF = 0.99295; $r = 0.9963$	$\ln \eta = K_7 C^{A_7} + K_{10} \exp(A_{10} C)/T + K_{12} \exp(A_{12} C)/T^2$ $K_7 = -2.91577 \text{ (kg/m}^3)^{-A_7}$ $A_7 = -0.000403 (-)$ $K_{10} = 1068.279 \text{ K}$ $A_{10} = 0.006981 \text{ (kg/m}^3)^{-1}$ $K_{12} = 6.443368 \text{ K}^2$ $A_{12} = -4.82281 \text{ (kg/m}^3)^{-1}$ RMSE = 0.005892; MBE = -0.00068 MPE = -0.02097; $\chi^2 = 0.002182$ EF = 0.99058; $r = 0.9956$	$\ln \eta = K_8 \exp(A_8 C) + K_9 C^{A_9}/T + K_{11} C^{A_{11}}/T^2$ $K_8 = -2.81916 (-)$ $A_8 = 0.003166 \text{ (kg/m}^3)^{-1}$ $K_9 = 1049.787 \text{ K (kg/m}^3)^{-A_9}$ $A_9 = 0.012397 (-)$ $K_{11} = 294.6172 \text{ K}^2 \text{ (kg/m}^3)^{-A_{11}}$ $A_{11} = 1.835890 (-)$ RMSE = 0.005786; MBE = -0.00037 MPE = -0.01735; $\chi^2 = 0.001628$ EF = 0.992972; $r = 0.9964$
Model 10	Model 11	Model 12
$\ln \eta = K_8 \exp(A_8 C) + K_9 C^{A_9}/T + K_{12} \exp(A_{12} C)/T^2$ $K_8 = -3.00819 (-)$ $A_8 = -0.00815 \text{ (kg/m}^3)^{-1}$ $K_9 = 1096.66 \text{ K (kg/m}^3)^{-A_9}$ $A_9 = 0.001664 (-)$ $K_{12} = 36.06507 \text{ K}^2$ $A_{12} = -7.03621 \text{ (kg/m}^3)^{-1}$ RMSE = 0.005786; MBE = -0.00037 MPE = -0.01735; $\chi^2 = 0.001628$ EF = 0.992972; $r = 0.9964$	$\ln \eta = K_8 \exp(A_8 C) + K_{10} \exp(A_{10} C)/T + K_{11} C^{A_{11}}/T^2$ $K_8 = -2.79445 (-)$ $A_8 = 0.10453 \text{ (kg/m}^3)^{-1}$ $K_{10} = 1031.366 \text{ K}$ $A_{10} = 0.015375 \text{ (kg/m}^3)^{-1}$ $K_{11} = 121.5429 \text{ K}^2 \text{ (kg/m}^3)^{-A_{11}}$ $A_{11} = 0.563581$ RMSE = 0.007002; MBE = -0.00042 MPE = -0.01912; $\chi^2 = 0.001805$ EF = 0.992206; $r = 0.99597$	$\ln \eta = K_8 \exp(A_8 C) + K_{10} \exp(A_{10} C)/T + K_{12} \exp(A_{12} C)/T^2$ $K_8 = -2.79641 (-)$ $A_8 = 0.10492 \text{ (kg/m}^3)^{-1}$ $K_{10} = 1032.271 \text{ K}$ $A_{10} = 0.015503 \text{ (kg/m}^3)^{-1}$ $K_{12} = -15.3782 \text{ K}^2$ $A_{12} = -12.6819 \text{ (kg/m}^3)^{-1}$ RMSE = 0.006968; MBE = -0.00042 MPE = -0.01915; $\chi^2 = 0.001805$ EF = 0.992189; $r = 0.99596$
Model 13	Model 14	Model 15
$\ln \eta = K_7 C^{A_7} + K_9 C^{A_9}/T + K_{11} C^{A_{11}}/T$ $K_7 = -65.0739 \text{ (kg/m}^3)^{-A_7}$ $A_7 = -0.559531 (-)$ $K_9 = 10714.71 \text{ K (kg/m}^3)^{-A_9}$ $A_9 = -0.48862 (-)$ $K_{11} = -0.1 \text{ K}^{-1} \text{ (kg/m}^3)^{-A_{11}}$ $A_{11} = -0.624085 (-)$ RMSE = 0.032272; MBE = 0.002768 MPE = -0.05227; $\chi^2 = 0.069389$ EF = 0.700434; $r = 0.85728$	$\ln \eta = K_7 C^{A_7} + K_9 C^{A_9}/T + K_{12} \exp(A_{12} C)/T$ $K_7 = 0.729085 \text{ (kg/m}^3)^{-A_7}$ $A_7 = -2.16055 (-)$ $K_9 = 128.5243 \text{ K (kg/m}^3)^{-A_9}$ $A_9 = -0.290416 (-)$ $K_{12} = -0.059905 \text{ K}^{-1}$ $A_{12} = -3.61843 \text{ (kg/m}^3)^{-1}$ RMSE = 0.065273; MBE = -0.01808 MPE = 1.80792; $\chi^2 = 0.110905$ EF = 0.521203; $r = 0.73$	$\ln \eta = K_7 C^{A_7} + K_{10} \exp(A_{10} C)/T + K_{11} C^{A_{11}}/T$ $K_7 = -65.5434 \text{ (kg/m}^3)^{-A_7}$ $A_7 = -0.013561 (-)$ $K_{10} = 10558.32 \text{ K}$ $A_{10} = 0.00547 \text{ (kg/m}^3)^{-1}$ $K_{11} = 0.102989 \text{ K}^{-1} \text{ (kg/m}^3)^{-A_{11}}$ $A_{11} = -0.027686 (-)$ RMSE = 0.003313; MBE = 0.005115 MPE = -0.05695; $\chi^2 = 0.048984$ EF = 0.788528; $r = 0.89699$
Model 16	Model 17	Model 18
$\ln \eta = K_7 C^{A_7} + K_{10} \exp(A_{10} C)/T + K_{12} \exp(A_{12} C)/T$ $K_7 = 4.236101 \text{ (kg/m}^3)^{-A_7}$	$\ln \eta = K_8 \exp(A_8 C) + K_9 C^{A_9}/T + K_{11} C^{A_{11}}/T$ $K_8 = -10.2260 (-)$	$\ln \eta = K_8 \exp(A_8 C) + K_9 C^{A_9}/T + K_{12} \exp(A_{12} C)/T$ $K_8 = 3.76368 (-)$

(continued on next page)

Table 2 (continued)

Model 1	Model 2	Model 3
$A_7 = 0.001947 (-)$ $K_{10} = -540.653 \text{ K}$ $A_{10} = -66.4586 (\text{kg/m}^3)^{-1}$ $K_{12} = -0.011918 \text{ K}^{-1}$ $A_{12} = -0.006360 (\text{kg/m}^3)^{-1}$ $\text{RMSE} = 0.004461; \text{MBE} = -0.00162$ $\text{MPE} = -0.03473; \chi^2 = 0.004475$ $\text{EF} = 0.980682; r = 0.99265$	$A_8 = -10.4319 (\text{kg/m}^3)^{-1}$ $K_9 = 115.9016 \text{ K} (\text{kg/m}^3)^{-A_9}$ $A_9 = -0.327326 (-)$ $K_{11} = 0.000598 \text{ K}^{-1} (\text{kg/m}^3)^{-A_{11}}$ $A_{11} = -0.805521 (-)$ $\text{RMSE} = 0.114543; \text{MBE} = -0.04582$ $\text{MPE} = -1.11639; \chi^2 = 0.341248$ $\text{EF} = 0.152588; r = 0.572$	$A_8 = -0.058155 (\text{kg/m}^3)^{-1};$ $K_9 = 70.6174 \text{ K} (\text{kg/m}^3)^{-A_9}$ $A_9 = 0.754124 (-)$ $K_{12} = -0.010593 \text{ K}^{-1}$ $A_{12} = -0.023247 (\text{kg/m}^3)^{-1}$ $\text{RMSE} = 0.09191; \text{MBE} = -0.00069$ $\text{MPE} = -0.01968; \chi^2 = 0.002059$ $\text{EF} = 0.991111; r = 0.99592$
Model 19	Model 20	Model 21
$\ln \eta = K_8 \exp(A_8 C) + K_{10} \exp(A_{10} C)/T$ $+ K_{11} C^{A_{11}} T$ $K_8 = 1.072311 (-)$ $A_8 = -0.046217 (\text{kg/m}^3)^{-1}$ $K_{10} = 450.5706 \text{ K}$ $A_{10} = 0.031384 (\text{kg/m}^3)^{-1}$ $K_{11} = -0.006313 \text{ K}^{-1} (\text{kg/m}^3)^{-A_{11}}$ $A_{11} = -0.019270 (-)$ $\text{RMSE} = 0.005912; \text{MBE} = -0.0066$ $\text{MPE} = -0.01939; \chi^2 = 0.001964$ $\text{EF} = 0.99152; r = 0.99608$	$\ln \eta = K_8 \exp(A_8 C) + K_{10} \exp(A_{10} C)/T$ $+ K_{12} \exp(A_{12} C) T$ $K_8 = 3.9400973$ $A_8 = 0.018432 (\text{kg/m}^3)^{-1}$ $K_{10} = 1.04985 \text{ K}$ $A_{10} = -32.4659 (\text{kg/m}^3)^{-1}$ $K_{12} = -0.10957 \text{ K}^{-1}$ $A_{12} = 0.014926 (\text{kg/m}^3)^{-1}$ $\text{RMSE} = 0.009576; \text{MBE} = -0.0083$ $\text{MPE} = -0.02332; \chi^2 = 0.002501$ $\text{EF} = 0.989201; r = 0.99551$	$\log \eta = K_7 C^{A_7}/T - K_9 C^{A_9}$ $K_7 = 450.1556 \text{ K} (\text{kg/m}^3)^{-A_7}$ $A_7 = 0.064510 (-)$ $K_9 = 1.207493 (\text{kg/m}^3)^{-A_9}$ $A_9 = 0.052755 (-)$ $\text{RMSE} = 0.021316; \text{MBE} = -0.00115$ $\text{MPE} = -0.04923; \chi^2 = 0.005387$ $\text{EF} = 0.975451; r = 0.98906$
Model 22	Model 23	Model 24
$\log \eta = K_7 C^{A_7}/T - K_{10} \exp(A_{10} C)$ $K_7 = 78.45376 \text{ K} (\text{kg/m}^3)^{-A_7}$ $A_7 = 0.129111 (-)$ $K_{10} = -0.079965 (-)$ $A_{10} = -3.649932 (\text{kg/m}^3)^{-1}$ $\text{RMSE} = 0.096295; \text{MBE} = -0.02154$ $\text{MPE} = -2.25707; \chi^2 = 0.124844$ $\text{EF} = 0.431082; r = 0.65588$	$\log \eta = K_8 \exp(A_8 C)/T - K_9 C^{A_9}$ $K_8 = 463.9447 \text{ K}$ $A_8 = 0.006982 (\text{kg/m}^3)^{-1}$ $K_9 = 1.266301 (\text{kg/m}^3)^{-A_9}$ $A_9 = -0.000401 (-)$ $\text{RMSE} = 0.005891; \text{MBE} = -0.00068$ $\text{MPE} = -0.002097; \chi^2 = 0.002068$ $\text{EF} = 0.990558; r = 0.99557$	$\log \eta = K_8 \exp(A_8 C)/T - K_{10} \exp(A_{10} C)$ $K_8 = 448.3102 \text{ K}$ $A_8 = -0.015503 (\text{kg/m}^3)^{-1}$ $K_{10} = 1.214470$ $A_{10} = 0.010492 (\text{kg/m}^3)^{-1}$ $\text{RMSE} = 0.006969; \text{MBE} = -0.00042$ $\text{MPE} = -0.01914; \chi^2 = 0.001714$ $\text{EF} = 0.992189; r = 0.99596$
Model 25	Model 26	Model 27
$\eta = K_7 C^{A_7} - K_9 C^{A_9} \log T$ $K_7 = 38.62725 (\text{kg/m}^3)^{-A_7}$ $A_7 = 0.117354 (-)$ $K_9 = 14.78417 (\text{kg/m}^3)^{-A_9}$ $A_9 = 0.119098 (-)$ $\text{RMSE} = 0.031114; \text{MBE} = -0.0003$ $\text{MPE} = -0.03469; \chi^2 = 0.008827$ $\text{EF} = 0.959774; r = 0.97968$	$\eta = K_7 C^{A_7} - K_{10} \exp(A_{10} C) \log T$ $K_7 = 42.79103 (\text{kg/m}^3)^{-A_7}$ $A_7 = -0.000797 (-)$ $K_{10} = -16.49081 (-)$ $A_{10} = -0.001562 (\text{kg/m}^3)^{-1}$ $\text{RMSE} = 0.011357; \text{MBE} = -0.00128$ $\text{MPE} = 0.074121; \chi^2 = 0.008944$ $\text{EF} = 0.959237; r = 0.97941$	$\eta = K_8 \exp(A_8 C) - K_9 C^{A_9} \log T$ $K_8 = 41.98693 (-)$ $A_8 = 0.001168 (\text{kg/m}^3)^{-1}$ $K_9 = 16.15891 (\text{kg/m}^3)^{-A_9}$ $A_9 = -0.000142 (-)$ $\text{RMSE} = 0.005866; \text{MBE} = -0.00296$ $\text{MPE} = -0.057846; \chi^2 = 0.00874$ $\text{EF} = 0.960173; r = 0.97988$
Model 28		
$\eta = K_8 \exp(A_8 C) - K_{10} \exp(A_{10} C) \log T$ $K_8 = 36.18997 \text{ mPa s}; A_8 = -0.41134 (\text{kg/m}^3)^{-1}; K_{10} = 1,338,019 (-); A_{10} = 0.041848 (\text{kg/m}^3)^{-1}$ $\text{RMSE} = 0.020188; \text{MBE} = 0.0000232; \text{MPE} = -0.00339; \chi^2 = 0.004378; \text{EF} = 0.980049; r = 0.98977$		

(-): dimensionless; η : mPa s; T : K; C : (kg/m^3).

where η is the viscosity of cellulose solution (mPa s), η_0 is a preexponential factor (mPa s), E_a is the activation energy of flow (kJ/mol), R is the gas constant (8.314×10^{-3} kJ/mol K), T is the absolute temperature (K) and A, B, C are constants.

The variation of viscosity with concentration can be described by either a power-type or an exponential-type relationship (Ibarz, Pagan, & Miguelsanz, 1992)

$$\eta = K_1(C)A_1 \quad (14)$$

$$\eta = K_2 \exp(A_2 C) \quad (15)$$

In both equations, K_1 (mPa s (kg/m^3) $^{-A_1}$), K_2 (mPa s), A_1 (dimensionless) and A_2 (kg/m^3) $^{-1}$ are constants and C is the concentration of cellulose solutions (kg/m^3).

Variation of E_a , η_0 , A, B and C constants in Eqs. (9)–(13) with concentration can be described by the following equations.

$$\eta = K_3(C)^{A_3} \quad (16)$$

$$\eta_0 = K_4 \exp(A_4 C) \quad (17)$$

$$E_a = K_5(C)^{A_5} \quad (18)$$

$$E_a = K_6 \exp(A_6 C) \quad (19)$$

$$A = K_7(C)^{A_7} \quad (20)$$

$$A = K_8 \exp(A_8 C) \quad (21)$$

$$B = K_9(C)^{A_9} \quad (22)$$

$$B = K_{10} \exp(A_{10} C) \quad (23)$$

$$C = K_{11}(C)^{A_{11}} \quad (24)$$

$$C = K_{12} \exp(A_{12} C) \quad (25)$$

The effect of temperature and concentration on viscosity could be combined into a single equation. Such a relationship can be used to model viscosity in operations where both the temperature and concentration change during the process. Twenty-eight different theoretical models were derived by combining Eqs. (9)–(13) and (16)–(25). Empirical relations describing the temperature and concentration dependence of viscosity were fitted to the experimental data and the constants in equations were determined by multiple regression analysis of the experimental data in the temperature range 10–60 °C and in the concentration range 0.5–10 kg/m³. The regression analyses were done by using the STATISTICA routine. The various statistical parameters such as mean percentage error (MPE), mean bias error (MBE), root mean square error (RMSE), modelling efficiency (EF) and chi-square χ^2 were used to determine the quality of the fit. Table 2 shows the values of the obtained constants and summary of the statistical analysis.

As seen from Table 2 MPE, MBE, RMSE, χ^2 values of models (1–10) derived by combining Eqs. (9) and (10) were lower than models (11–28) derived by combining Eqs. (11)–(13). Since model 6 has the lowest MPE, MBE, RMSE, χ^2 values and the highest EF and regression coefficient values, it can be used to predict viscosity in operations where both the temperature and concentration change during the process. The combined effect of temperature and concentration on the viscosity of cellulose from sugar beet pulp can be modelled by the equation (model 6) derived by combining Eqs. (10), (20), (22) and (25). A multiple regression analysis on the viscosity–concentration–temperature data showed that the following equation could be proposed to evaluate the viscosity of cellulose from sugar beet pulp for the concentrations and temperatures studied

$$\ln \eta = -2.8C^{0.0186} + 1031C^{0.025}/T + 2654 \exp(0.1896C)/T^2 \quad (26)$$

χ^2 and EF values of models (1–10) are shown in Fig. 4. Model 6 has the lowest χ^2 value and the highest EF value between models (1–10).

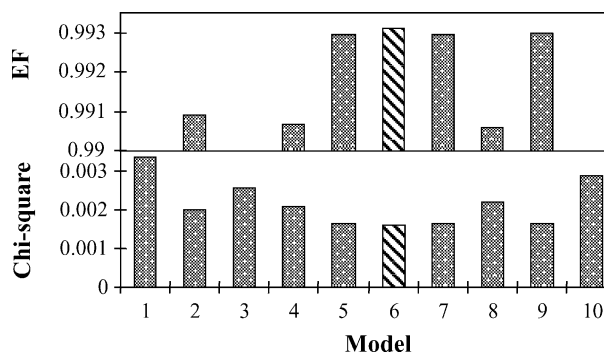


Fig. 4. χ^2 and EF values of models.

Fig. 5 shows the variation of the viscosity calculated by using model 6 with concentration and temperature.

Fig. 6 shows the relationship between the experimental viscosity and the viscosity calculated by using model 6.

The pooled data for viscosity calculated by the model 6 versus experimental values shows an overall uniform good distribution of data points along the perfect diagonal line ($r^2 : 0.9928$).

It should be emphasized that the constants in Table 2 are applicable only to the range of temperatures and concentrations studied. The model will be useful for the applications of cellulose from sugar beet pulp.

3.2. Intrinsic viscosity–average molecular weight relationship

Intrinsic viscosity, a measure of the hydrodynamic volume occupied by a molecule, is a measure of the capacity of a polymer molecule to enhance the viscosity (Brandrup & Immergut, 1975). The intrinsic viscosities obtained by the plot of η_{sp}/c versus C for solutions prepared from cellulose extracted with 10% NaOH at 35 °C for times of 10, 16 and 22 h were 0.0357, 0.0578

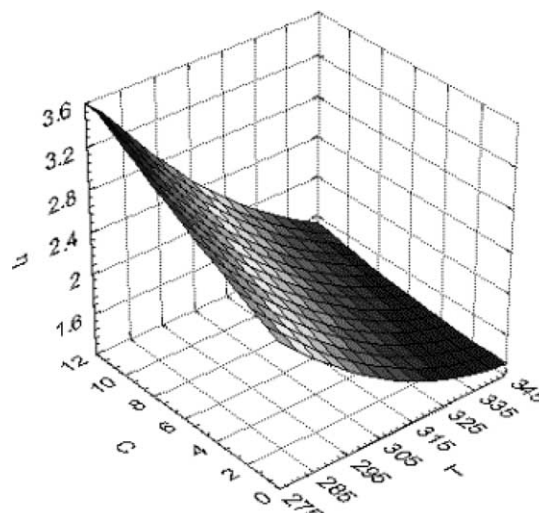


Fig. 5. Variation of the viscosity calculated by using model 6 with concentration and temperature.

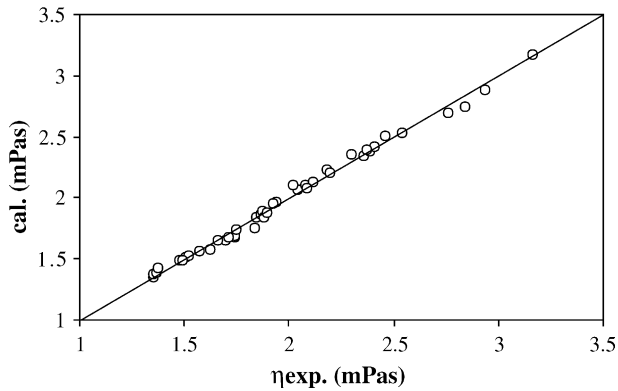


Fig. 6. Comparison of the experimental viscosity and the viscosity calculated by using model 6.

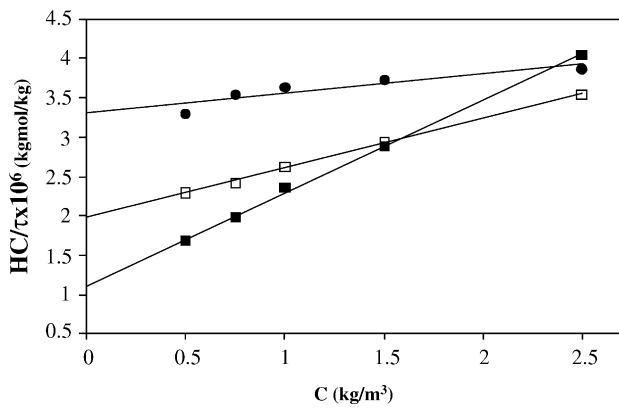


Fig. 7. Light-scattering determination of the molecular weight of cellulose from sugar beet pulp (time (h): ●, 10; □, 16; ■, 22).

and $0.0820 \text{ m}^3/\text{kg}$, respectively. The decrease in intrinsic viscosity means a decrease of the hydrodynamic volume of the macromolecular chain (Hirrien et al., 1996).

HC/τ values were calculated and plotted against concentration of cellulose solutions (Fig. 7).

Table 3
Data for calculating average molecular weight

Extraction conditions	$C \text{ (kg/m}^3\text{)}$	Optical rotation	Transmittance (%)	Turbidity $\tau \times 10^2 \text{ (m}^{-1}\text{)}$	$HC/\tau \times 10^6 \text{ (kg mol/kg)}$	$M_{w,ave} \text{ (kg/kg mol)}$
10% NaOH, 35 °C, 10 h	0.50	1.4091	54	0.46	3.290	303,200
	0.75	1.4103	43	0.57	3.538	
	1.00	1.4112	38	0.62	3.628	
	1.50	1.4128	30	0.70	3.733	
	2.50	1.4151	28	0.72	3.871	
10% NaOH, 35 °C, 16 h	0.50	1.4084	60	0.40	2.292	520,400
	0.75	1.4095	45	0.55	2.419	
	1.00	1.4105	38	0.62	2.628	
	1.50	1.4122	30	0.70	2.941	
	2.50	1.4150	26	0.74	3.538	
10% NaOH, 35 °C, 22 h	0.50	1.4077	76	0.24	1.687	893,500
	0.75	1.4086	67	0.33	1.974	
	1.00	1.4097	55	0.45	2.345	
	1.50	1.4118	38	0.62	2.894	
	2.50	1.4155	24	0.76	4.043	

HC/τ versus C showed similar trends and straight lines with linear regression coefficients in the range 0.99–1.0. The reciprocal of the intercept is the average molecular weight. The results are presented in Table 3.

Intrinsic viscosity is a characteristic of macromolecules that is related directly to their ability to disturb flow and indirectly to their size and shape. For molecules that can exist with a variety of molecular weights, the relation between intrinsic viscosity and molecular weight is one of the most important properties (Johnston & Sourirajan, 1973). The intrinsic viscosity as functions of average molecular weight are usually represented by widely used Mark-Houwink-Sakurada empirical equations (Isihara, 1992):

$$\eta_i = K(M_{w,ave})^\alpha \quad (27)$$

Both the exponent α and K are constants. These constants are dependent on the nature of the molecule and solvent, and on the temperature (Tanglerpaibul & Rao, 1987).

The equation may be written as follows:

$$\ln \eta_i = \ln K + \alpha \ln M_{w,ave} \quad (28)$$

Intrinsic viscosity values were used for plot of $\ln \eta_i$ versus $\ln M_{w,ave}$. The slope of the straight line obtained by Eq. (28) is α and its point of intersection with ordinate gives $\ln K$. From this graph, K and α were found to be $2.313 \times 10^{-6} \text{ m}^3/\text{kg}$ and 0.7665, respectively. The viscometric average molecular weight can be estimated according to the relation:

$$\eta_i = 2.313 \times 10^{-6} (M_{w,ave})^{0.7665} \quad (29)$$

The constants of Eq. (29) are applicable for cellulose solutions in 37% HCl solvent alone. Eq. (29) helps to evaluate the average molecular weight of cellulose solutions from sugar beet pulp with knowledge of their intrinsic viscosity and α, K coefficients.

References

- Abramovic, H., & Klofutar, L. (1998). The temperature dependence of dynamic viscosity for some vegetable oils. *Acta Chimica Slovenica*, 45(1), 69–77.
- Allock, H. R., & Lampe, F. W. (1981). In *Contemporary polymer chemistry*. Englewood Cliffs, NJ: Prentice-Hall.
- AOAC (1984). *Official methods of analysis* (14th ed). Washington, DC: Association of Official Analytical Chemists.
- Brandrup, J., & Immergut, E. H. (1975). In *Polymer handbook* (2nd ed). New York: Wiley.
- Chamberlain, E. K., & Rao, M. A. (2000). Effect of concentration on rheological properties of acid-hydrolysed amylopectin solutions. *Food Hydrocolloid*, 14, 163–171.
- Constella, D. T., Lozano, J. E., & Crapiste, G. H. (1989). Thermophysical properties of clarified apple juice as a function of concentration and temperature. *Journal of Food Science*, 54(3), 663–668.
- Coughlan, M. P., Mehra, R. K., Considine, P. J., O'Rourke, A., & Puls, J. (1985). Saccharification of agricultural residues by combined cellulolytic and pectinolytic enzyme systems. *Biotechnology Bioengineering Symposium*, 15, 447–458.
- Hirrien, M., Desbrieres, J., & Rinaudo, M. (1996). Physical properties of methylcelluloses in relation with the conditions for cellulose modification. *Carbohydrate Polymers*, 31, 243–252.
- Howard, D. W. (1991). A look at viscometry. *Food Technology*, 45, 82–84.
- Ibarz, A., Pagan, J., & Miguelsanz, R. (1992). Rheology of clarified fruit juices. II. Blackcurrant juices. *Journal of Food Engineering*, 15, 63–73.
- Isihara, A. (1992). On the viscosity of chain polymers. *Polymer*, 33(1), 111–112.
- Johnston, H. K., & Sourirajan, S. (1973). Viscosity–temperature relationships for cellulose acetate–acetone solutions. *Journal of Applied Polymer Science*, 17, 3717–3726.
- Kar, F., & Arslan, N. (1999). Effect of temperature and concentration on viscosity of orange peel pectin solutions and intrinsic viscosity–molecular weight relationship. *Carbohydrate Polymers*, 40, 277–284.
- Kennedy, J. F., Rivera, Z. S., Lloyd, L. L., Warner, F. P., & Silva, M. P. C. (1995). Determination of the molecular weight distribution of hydroxyethylcellulose by gel permeation chromatography. *Carbohydrate Polymers*, 26, 31–34.
- Kirk, R. E., & Othmer, D. F. (1967). Cellulose. *Encyclopedia of Chemical Technology*, 4, 593–683.
- Kirk, D. E., & Othmer, D. F. (1970) (2nd ed) (vol. 21). *Encyclopedia of chemical technology*, New York: Wiley.
- Ng, W. K., Tam, K. C., & Jenkins, R. D. (1999). Evaluation of intrinsic viscosity measurements of hydrophobically modified polyelectrolyte solutions. *European Polymer Journal*, 35, 1245–1252.
- Ott, E. (1946). In *Cellulose and cellulose derivatives*. New York: Interscience Publishers.
- Pagan, J., & Ibarz, A. (1999). Extraction and rheological properties of pectin from fresh peach pomace. *Journal of Food Engineering*, 39, 193–201.
- Pang, S., & Rudin, A. (1992). Use of continuous viscometer and light scattering detectors in characterization of polyolefins: comparisons of data from individual and combined detectors. *Journal of Applied Polymer Science*, 46, 763–773.
- Rao, D. G. (1993). Studies on viscosity–molecular weight relationship of chitosan solutions. *Journal of Food Science Technology*, 30, 66–67.
- Rao, M. A., & Anantheswaran, R. C. (1982). Rheology of fluid in food processing. *Food Technology*, 36(2), 116–126.
- Rao, M., Cooley, M. J., & Vitali, A. A. (1984). Flow properties of concentrated juices at low temperatures. *Food Technology*, 38(3), 113–119.
- Sun, R. C., Fang, J. M., Tomkinson, J., Geng, Z. C., & Liu, J. C. (2001). Fractional isolation, physico-chemical characterization and homogeneous esterification of hemicelluloses from fast-growing poplar wood. *Carbohydrate Polymers*, 44, 29–39.
- Sun, R., & Hughes, S. (1998). Fractional extraction and physicochemical characterization of hemicelluloses and cellulose from sugar beet pulp. *Carbohydrate Polymers*, 36, 293–299.
- Tanglertpaibul, T., & Rao, M. A. (1987). Intrinsic viscosity of tomato serum as affected by methods of determination and methods of processing concentrates. *Journal of Food Science*, 52, 1642–1645.
- Wen, L. F., Chang, K. C., & Gallaher, D. D. (1988). Isolation and characterization of hemicellulose and cellulose from sugar beet pulp. *Journal of Food Science*, 53(3), 826–829.