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Production of carboxymethyl cellulose from sugar beet pulp cellulose and rheological behaviour of carboxymethyl cellulose

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Abstract

The sugar beet pulp cellulose was converted carboxymethyl cellulose (CMC) by etherification and the process of carboxymethylation was optimised with respect to the solvent medium, alkali concentration, sodium chloroacetate amount, temperature and time of reaction. The optimised product had a DS of 0.6670 and the optimum conditions for carboxymethylation were sodium chloroacetate amount of 3.0 g, an NaOH concentration of 30%, temperature of 70 °C, time of 360 min with isobutyl alcohol as the solvent medium. The flow behaviour of CMC from sugar beet pulp cellulose was determined using a rotational viscometer for concentration range of 10–30 kg/m^3, temperature range of 20–30 °C, and shear rate range of 3.24–64.8 s^{-1}. Newtonian, Bingham and power law models were applied to fit the flow behaviour of CMC solutions. The behaviour of CMC solutions was pseudoplastic and the flow behaviour of CMC solutions was found to be most adequately described by the power-law model. Concentration, temperature and shear rate affected the rheological properties. The temperature dependency of the consistency coefficient and the flow behaviour index was modelled using a Turian approach. Both the consistency coefficient and the flow behaviour index were sensitive to changes in temperature and concentration. The consistency coefficient varied between 0.0024 and 0.0162 whereas the flow behaviour index varied between 0.7017 and 0.9590. The flow behaviour index decreased with concentration and increased with temperature, while the opposite trend was observed with the consistency coefficient. The apparent viscosity decreased with increasing temperature and shear rate implying that CMC solutions studied behaved as shear thinning. The experimental data were fitted by mathematical models to allow prediction of the consistency coefficient, the flow behaviour index and the apparent viscosity as a function of temperature and concentration.

Keywords: Sugar beet pulp; Cellulose; Carboxymethylation; Carboxymethyl cellulose; Rheology

1. Introduction

Sugar beet pulp (SBP) is a by-product from the beet sugar industry. SBP has been reported to contain large amounts of cellulose (Wen, Chang, & Gallaher, 1988). Cellulose might be converted to useful derivatives by etherification (Kirk & Othmer, 1967). Carboxymethyl cellulose (CMC) is the most important water-soluble cellulose derivative, with many applications in the food industry and in cosmetics, pharmaceuticals, detergents, etc. (Olaru, Olaru, Stoleriu, & Timpu, 1998). Na CMC is a copolymer of two units: β-D-glucose and β-D-glucopyranose 2-*O*-(carboxymethyl)-monosodium salt, not randomly distributed along the macromolecule, which are linked via β-1,4-glycosidic bonds. The substitution of the hydroxyl groups by the carboxymethyl group is slightly preponderant at C-2 of the glucose (Charpentier et al., 1997). Production of CMC is carried out by conversion of alkali cellulose swollen in aqueous NaOH and a surplus of an organic solvent with monochloroacetic acid or its sodium salt (Heinze & Pfeiffer, 1999).

It is necessary accurate data on rheological properties for design of food processing operations such as mixing, pumping, heating and cooling. Flow characteristics of a pumpable food product are dependent on the fluid rheology (Abdelrahim & Ramaswamy, 1995). With regard to engineering calculations, knowledge of the applicable flow models is important for design of flow systems (Rao & Anantheswaran, 1982). Designing equipment for fluid flow and heat transfer operations which are involved in using CMC solutions at different concentrations requires data on knowledge of the rheological properties of CMC solutions. Concentration, temperature, size distribution, particle

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shape, flexibility, electrical and surface properties and mode of interaction of the suspended particles considerably affect the flow behaviour. Moreover, soluble solids play a major role in determining the mode and extent of interparticle interaction and changes in pH markedly affect the zeta potential, influencing the rheological behaviour (Mizrahi, 1979). Different equations were used for the description of fluid: Newtonian model (Giner, Ibarz, Garza, & Xhian-Quan, 1996; Ibarz, Gonzales, & Esplugas, 1994; Khalil, Ramakrishna, & Patward-Han, 1989), Bingham model (Fichtali, Van De Voort, & Doyon, 1993; Ibarz, Garvin, & Costa, 1999), power law model (Ibarz & Pagan, 1987; Rao, Cooley, & Vitali, 1984; Vitali & Rao, 1982; Vitali, Roig, & Rao, 1974) and Herschel and Bulkley model (Guerrero & Alzamora, 1998; Marcotte, Taherian, Trigul, & Ramaswamy, 2001).

The objectives of this study were: (1) to examine carboxymethylation of cellulose obtained from SBP and effects of alkali concentration, acid concentration, solvent, temperature and time of reaction on degree of substitution (DS) of CMC, (2) to investigate the rheological behaviour of CMC solutions at various temperatures, concentrations and shear rates, and (3) to evaluate the combined effect of temperature and concentration on the power law parameters (m and n) and apparent viscosities of CMC solutions.

2. Materials and methods

2.1. Production of CMC from SBP cellulose

Two grams of cellulose from SBP in optimised cellulose extraction conditions (Toğrul & Arslan, 2003), 100 ml of solvent (water, ethanol, isopropyl alcohol and isobutyl alcohol) and 20 ml of NaOH having concentrations of 5, 10, 15, 20, 25 and 30% were mechanically stirred for 90 min at 25 °C in a reaction vessel with the heat stabilization jacket. The mixture was filtered to a weight of about 6.5 g and shredded for 90 min in a shredder. Then 1.0, 1.4, 1.8, 2.2, 2.6 and 3.0 g of sodium chloroacetate (SCA) are added and shredding was continued at temperatures of 30, 40, 50, 60 and 70 °C and times of 60, 90, 120, 180 and 360 min. Water from a constant temperature bath was circulated through the jacket of the reaction vessel to maintain the constant the temperature during carboxymethylation. After the time of reaction was finished, the mixture was neutralized with the acetic acid of 90% and filtered. Cake was purified by washing with 70% methanol to remove undesired salts, filtered and dried at 70 °C (Kirk & Othmer, 1967).

Moisture content of CMC was determined by using the method 40-40 of AACC (1983). The DS of CMC was determined by the standard method (ASTM, 1961). Using methanol 108 ml of 65% HNO_3 was made to one litre. 5 g of CMC was shaken with 200 ml of HNO_3–methanol mixture, kept for 3 h and the surplus acid was washed with 70% methanol. Two grams of dried CMC was added to 200 ml of distilled water and 30 ml of 1N NaOH. After dissolved, the mixture was titrated by 1N HCl. The DS of CMC was determined by following equations (ASTM, 1961; Barai, Singhal, & Kulkarni, 1997)

$$\mathrm{DS} = 0.162A/(1 - 0.058A)$$

$$A = (BC - DE)/F$$

where A is the equivalent weight of alkali required per gram of sample; B (ml), the amount of NaOH solution; C, the normality of NaOH solution; D (ml), the amount of HCl solution; E, the normality of HCl solution; F (g) is the weight of sample.

To determine CMC content, 1.5 g of CMC was added to 100 ml of 80% methanol, stirred, kept for 10 min and filtered. Cake was washed by 100 ml of 80% methanol and dried (Far, 1992)

$$\text{CMC content\%} = 100m_2/m_1$$

where m_1 (g) is the weight of dried sample and m_2 (g) is the weight of washed sample.

To determine NaCl amount, 2 g of CMC was added to 250 ml of 65% methanol and kept for 5 h. 100 ml of liquid phase was neutralized by diluted HNO_3 and titrated by 0.1N $AgNO_3$ solution (Far, 1992).

$$\text{NaCl\%} = 1.461V/m$$

where V (ml) is the amount of $AgNO_3$ and m (g) is the weight of dried sample.

2.2. Rheological measurement

For rheological measurements, CMC solutions (5, 10, 15, 20, 25 and 30 kg/m^3) were prepared using CMC obtained at optimum carboxymethylation conditions. CMC solutions were prepared by hydrating in distilled water for overnight followed by vigorous mixing and standing for 24 h to release air bubbles. Solutions were carefully mixed before rheological measurements to avoid air entrapment.

Rheological measurements of CMC solutions were carried out using a model NDJ rotational viscometer equipped with a torque measuring head and a rotor. Samples of CMC were filled into the cylindrical cup and allowed to rest for 15 min to equilibrate to the desired temperature preset in the circulating bath. Experiments were performed at 20, 22, 25, 27, and 30 °C temperatures and concentrations of 5, 10, 15, 20, 25 and 30 kg/m^3 and the measurements were repeated three times and the average values were used to calculate the apparent viscosity. Coefficients of variation of the means were less than 5% for all repetition experiments. Speeds of the rotating inner cylinder varied from 3 to 60 rpm. Speeds were changed stepwise with a selector switch. The inner cylinder (rotor) has a radius of 12.5×10^{-3} m and a height of 9.1×10^{-2} m, while the outer cylinder has a radius of 14×10^{-3} m. Readings of torque were taken at increasing rotor speeds. Glycerol of 60% (w/w) was used to calibrate the rheometer.

2.3. Data analysis

The mechanical torque was converted to shear stress by using the following relation

$$\tau_{r\phi} = M_d/2\pi L R_0^2 \tag{1}$$

where $\tau_{r\phi}$ is the shear stress (Pa); M_d, the torque (Nm); R_0, the rotor radius (m); L is the height of the inner cylinder (m).

Shear stress and rotor speed relations are given by the following equations (Denn, 1980; Hangen & Tung, 1976; Shoemaker, Lewis, & Tamura, 1987; Steffe, 1992)

$$\text{Newtonian}: \quad \tau_{r\phi} = \frac{4\pi\mu N}{(1-R^2)60} \tag{2}$$

$$\text{Bingham}: \quad \tau_{r\phi} = -\tau_0\left(2\frac{\ln R}{1-R^2}\right) + \frac{4\pi\mu_0 N}{(1-R^2)60} \tag{3}$$

power law :

$$\ln\tau_{r\phi} = \ln\left[m\left(\frac{4\pi}{n(1-R^{2/n})}\right)^n\right] + n\ln(N/60) \tag{4}$$

where R is the ratio of the rotor radius to the inner radius of outer cylinder and N is the rotor speed (rpm).

The values of the μ, μ_0, τ_0, m and n model parameters were determined using shear stress-rotor speed linear relationships. If $\tau_{r\phi}$ and ln $\tau_{r\phi}$ were plotted versus $N/60$ and ln(N/60), it can be seen that graphs should be a straight line. The values of the slopes and intercepts on graphs enable model parameters to be calculated. Rheograms were evaluated using the Newtonian, Bingham and power law models. Taking into consideration the model parameters calculated using experimental data, it was determined the best flow model for CMC solutions. The regression analysis were done by using the STATISTICA routine.

3. Results and discussion

3.1. Optimization of CMC production conditions

The DS is a major factor in the water solubility Na CMC, below approximately 0.4 the polymer is swellable but insoluble, above this the polymer is fully soluble with its hydroaffinity increasing with increasing DS (Waring & Parsons, 2001).

The effect of different reaction conditions on the substitution degree, CMC and NaCl contents are given in Table 1.

A maximum DS of 0.6670 was obtained with isobutyl alcohol as the solvent medium. The role of the solvent in the carboxymethylation reaction is to provide accessibility of the etherifying reagent to the reaction centres of the cellulose chain (Savage, Young, & Maasberg, 1954). The differences in the extent of carboxymethylation can be explained by taking into consideration their polarities. The polarity index of isobutyl alcohol is lowest and the reaction efficiency increases as the polarity of the solvent decreases

Table 1
Effect of different reaction conditions on the substitution degree, CMC and NaCl contents

Conditions of carboxymethylation	Solvent	NaOH%	Time (min)	T (°C)	SCA amount (g)	DS	CMC%	NaCl%	Others%
Solvent	Water	30	60	30	3.0	0.1020	51.2	3.13	45.67
	Ethyl alcohol	30	60	30	3.0	0.1160	54.6	2.92	42.48
	Isopropyl alcohol	30	60	30	3.0	0.3270	57.0	2.55	40.45
	Isobutyl alcohol	30	60	30	3.0	0.4320	61.4	2.38	36.22
NaOH conc.	Isobutyl alcohol	5	60	30	3.0	0.1092	57.0	2.18	40.82
	Isobutyl alcohol	10	60	30	3.0	0.1799	68.0	2.11	29.89
	Isobutyl alcohol	15	60	30	3.0	0.2595	55.0	3.71	41.29
	Isobutyl alcohol	20	60	30	3.0	0.2803	56.1	2.72	41.18
	Isobutyl alcohol	25	60	30	3.0	0.3187	57.0	3.58	39.42
SCA	Isobutyl alcohol	30	60	30	1.0	0.1760	49.0	3.28	47.72
	Isobutyl alcohol	30	60	30	1.4	0.2630	54.0	4.08	41.92
	Isobutyl alcohol	30	60	30	1.8	0.4130	54.0	4.54	41.46
	Isobutyl alcohol	30	60	30	2.2	0.4220	57.0	3.28	39.72
	Isobutyl alcohol	30	60	30	2.6	0.4232	59.0	3.38	37.62
Time	Isobutyl alcohol	30	90	30	3.0	0.4818	60.4	3.65	35.95
	Isobutyl alcohol	30	120	30	3.0	0.5470	61.5	4.01	34.49
	Isobutyl alcohol	30	180	30	3.0	0.5890	60.2	4.38	35.42
	Isobutyl alcohol	30	360	30	3.0	0.6060	62.0	4.74	33.26
Temp.	Isobutyl alcohol	30	360	40	3.0	0.6110	63.0	4.74	32.26
	Isobutyl alcohol	30	360	50	3.0	0.6280	62.1	4.01	33.89
	Isobutyl alcohol	30	360	60	3.0	0.6560	64.0	3.58	32.42
	Isobutyl alcohol	30	360	70	3.0	0.6670	64.2	3.71	32.09

Table 2
Rheological model parameters constants as influenced by concentration and temperature

C (kg/m^3)	T (°C)	Newtonian model		Bingham model			Power law model			
		μ (mPa s)	r^2	μ_0 (mPa s)	τ_0 (Pa)	r^2	n	m (Pa s^n)	n_{ave}	r^2
5	20	2.352	0.9984	2.352	0.0075	0.9984	0.7981	0.0052	0.8870	0.9930
	22	2.272	0.9994	2.272	0.0058	0.9994	0.8390	0.0043		0.9974
	25	2.208	0.9982	2.208	0.0042	0.9982	0.8898	0.0035		0.9974
	27	2.190	0.9980	2.190	0.0039	0.9980	0.9491	0.0028		0.9914
	30	1.999	0.9992	1.999	0.0024	0.9992	0.9590	0.0024		0.9980
10	20	2.452	0.9990	2.452	0.0102	0.9990	0.7634	0.0064	0.7852	0.9938
	22	2.328	0.9984	2.328	0.0097	0.9984	0.7800	0.0057		0.9950
	25	2.191	0.9980	2.191	0.0094	0.9980	0.7836	0.0053		0.9968
	27	2.133	0.9986	2.133	0.0082	0.9986	0.7968	0.0049		0.9972
	30	1.972	0.9970	1.972	0.0091	0.9970	0.8022	0.0046		0.9984
15	20	3.208	0.9956	3.208	0.0205	0.9956	0.7294	0.0101	0.7473	0.9946
	22	2.971	0.9924	2.971	0.0187	0.9924	0.7347	0.0091		0.9908
	25	2.636	0.9964	2.636	0.0088	0.9964	0.7392	0.0072		0.9752
	27	2.250	0.9958	2.250	0.0123	0.9958	0.7575	0.0062		0.9972
	30	2.172	0.9964	2.172	0.0102	0.9964	0.7757	0.0055		0.9966
20	20	3.618	0.9982	3.618	0.0187	0.9982	0.7103	0.0116	0.7306	0.9872
	22	3.123	0.9954	3.123	0.0203	0.9954	0.7200	0.0102		0.9964
	25	2.459	0.9874	2.459	0.0202	0.9874	0.7301	0.0082		0.9976
	27	2.361	0.9960	2.361	0.0153	0.9960	0.7396	0.0072		0.9980
	30	2.274	0.9954	2.274	0.0130	0.9954	0.7531	0.0065		0.9956
25	20	3.986	0.9912	3.986	0.0286	0.9912	0.7095	0.0137	0.7274	0.9938
	22	3.556	0.9752	3.556	0.0308	0.9752	0.7114	0.0127		0.9944
	25	3.451	0.9932	3.451	0.0181	0.9932	0.7278	0.0104		0.9835
	27	3.112	0.9972	3.112	0.0159	0.9972	0.7386	0.0091		0.9890
	30	3.058	0.9986	3.058	0.0137	0.9986	0.7499	0.0084		0.9888
30	20	4.416	0.9888	4.416	0.0372	0.9888	0.7017	0.0162	0.7230	0.9988
	22	3.871	0.9866	3.871	0.0345	0.9866	0.7152	0.0138		0.9956
	25	3.555	0.9847	3.555	0.0287	0.9847	0.7251	0.0120		0.9986
	27	3.373	0.9934	3.373	0.0226	0.9934	0.7320	0.0106		0.9974
	30	3.057	0.9984	3.057	0.0170	0.9984	0.7407	0.0090		0.9966

(Barai et al., 1997). In a study of the carboxymethylation of wood pulp cellulose and cotton linters cellulose in different organic media, the ethanol-acetone mixture used as reaction medium was found to give a higher of DS (Olaru, Olaru, Stoleriu, & Timpu, 1998). Using isobutyl alcohol as the solvent medium, the effect of NaOH concentration on the DS was studied. DS increased with increasing NaOH concentration. Na CMC is prepared by treating alkali cellulose with sodium chloroacetate. A side reaction, the conversion of sodium chloroacetate to sodium glycolate, occurs simultaneously (Kirk & Othmer, 1967).

$$\mathrm{R_{cell}OH + NaOH \rightleftarrows R_{cell}OH{\cdot}NaOH}$$

$$\mathrm{R_{cell}OH{\cdot}NaOH + ClCH_2COONa \rightarrow R_{cell}OCH_2COONa + NaCl + H_2O}$$

$$\mathrm{NaOH + ClCH_2COONa \rightarrow HOCH_2COONa + NaCl}$$

DS increased with an increase in the sodium chloroacetate amount when used isobutyl alcohol as the solvent medium and a NaOH concentration of 30%. This may be due to the greater availability of the acid molecules at higher concentrations in the proximity of the cellulose molecules (Barai et al., 1997). If NaOH concentration and sodium chloroacetate amount is low, the side reaction predominates with the formation of larger amounts of sodium glycolate, thereby lowering the DS. There was a significant increase in the DS with temperature and time. The effect of time on DS was more in comparison with temperature. The increase in DS with temperature and time may be due to the fact that there is a better reaction environment created and a prolonged time available for carboxymethylation. This may lead to better reaction efficiency and higher DS of the final product (Barai et al., 1997). The optimised product had a DS of 0.6670 and the optimum conditions for carboxymethylation were sodium chloroacetate amount of 3.0 g, an NaOH concentration of 30%, temperature of 70 °C, time of 360 min with isobutyl alcohol as the solvent medium. CMC content increased but NaCl and sodium glycolate amounts decreased with increase in DS since the side reaction causes to decrease in DS.

3.2. Rheological behaviour

μ_0, τ_0, m and n parameters obtained from shear stress–rotor speed relationships are presented in Table 2.

The experimental results showed that the rheological behaviour of CMC (DS:0.6670) solutions was pseudoplastic and it was best fitted by the power law model since the values of τ_0 in Bingham model were nearly zero and the flow behaviour index (n) in power law model were less from 1.Values of n less than unity mean that CMC solutions exhibits a shear-thinning behaviour. Therefore, the power law model was used to characterize the flow behaviour of CMC solutions. Coefficients of determination (r^2) indicated a good fit for power law model. The flow behaviour index values ranged from 0.7017 to 0.9590 under different conditions of temperature and concentration, demonstrating the pseudoplastic character of CMC solutions. The degree of pseudoplasticity could be measured by the flow behaviour index (n), which decreases when pseudoplasticity increases. The highest and lowest values of n were observed at the lowest and highest CMC concentrations (5 and 30 kg/m^3, respectively), which indicate that non-Newtonian behaviour increases with increase of CMC concentration. The same relation was found by Mahmoud and Fugitt (1996) in a nutritional supplement of oat fibre, arabic gum and carboxymethyl cellulose. Abdelrahim and Ramaswamy (1995) examined the rheological behaviour of commercial CMC having concentrations of 0.5–2.0% and at 60–140 °C temperatures and explained that the rheological behaviour fitted by power law model for all CMC concentrations at 60 and 80 °C and at temperatures above 80 °C (0.5 and 1.0% CMC) and above 100 °C (1.5% CMC), the flow behaviour index was >1.0 indicating a dilatant flow behaviour. Westra (1989) stated that the rheological behaviour of CMC with xanthan gum was pseudoplastic. The shear rates ($-\mathrm{d}V_\phi/\mathrm{d}r$, s^{-1}) were calculated by the following equation using m and n values in Table 2.

$$\tau_{r\phi} = m(-\mathrm{d}V_\phi/\mathrm{d}r)^n \tag{5}$$

Fig. 1 shows a plot of shear stress versus shear rate for CMC solutions of 30 kg/m^3. Rheograms for other CMC concentrations show similar behaviour.

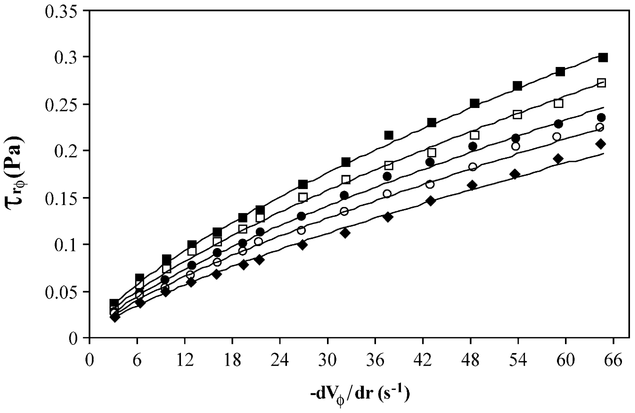


Fig. 1. Rheograms of CMC solutions of 30 kg/m^3 at different temperatures (in °C): ■, 20; □, 22; ●, 25; ○, 27; ◆, 30.

3.3. The combined effect of temperature and concentration on flow parameters

As seen from Table 2, the consistency coefficient (m) increased with concentration and decreased with temperature, while the opposite trend was observed with the flow behaviour index (n). This tendency was similar commercial CMC (Abdelrahim & Ramaswamy, 1995). The decrease of the m was more pronounced at higher concentrations. At a given temperature, that m increased as concentration increased was probably caused by the increase of particle-particle interaction. The degree of pseudoplasticity could be measured by the n that decreases when pseudoplasticity increases. The highest and lowest values of n were observed at the concentration of 5 kg/m^3, 30 °C temperature and the concentration of 30 kg/m^3 and 20 °C temperature respectively, which indicates that non-Newtonian behaviour increases with increase of amount of CMC in the solution. The consistency coefficient varied between 0.0024 and 0.0162 whereas the flow behaviour index varied between 0.7017 and 0.9590. It was reported that a non-Newtonian behaviour was more important when the flow behaviour index less than 0.6 (Muller, Pain, & Villon, 1994).

The effects of temperature and concentration on the m and n were shown for CMC solutions of 10–30 kg/m^3 since n values for CMC solutions of 5 kg/m^3 were near to 1. To study the effect of concentration in pseudoplasticity, it was calculated an average of n (n_{ave}) except for CMC solutions of 5 kg/m^3 (Table 2). Figs. 2 and 3 show the effects of temperature and concentration on the m and n of the samples and the relationship of average flow behaviour index and concentration, respectively.

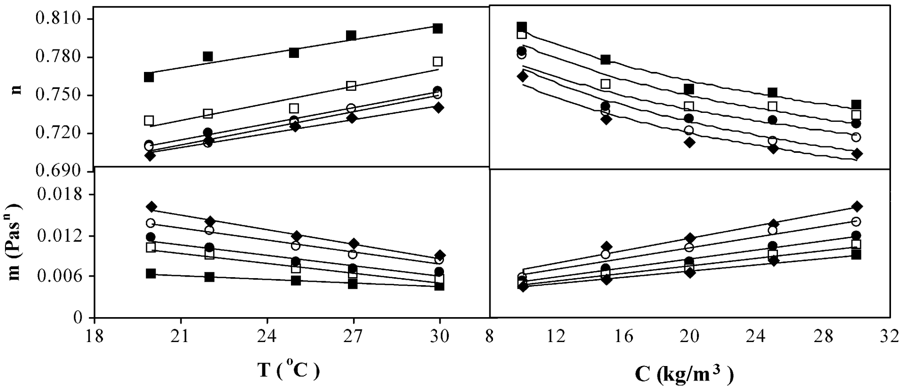
As seen from Fig. 3, there is a power-type relationship between the average n values and concentration.

The effects of temperature on the m and n are given by Turian approach (Turian, 1964)

$$\log m = \log m_0 - A_1 T \tag{6}$$

$$n = n_0 + A_2 T \tag{7}$$

It is evident that concentration had a considerable effect on the flow behaviour of CMC solutions. The variation of m and n with the concentration was described by power-law and exponential relationships (Guerrero & Alzamora, 1998; Jinescu, 1974; Khalil, Ramakrishna, Nanjundaswamy, & Patwardhan, 1989).



(a) (b)

Fig. 2. Effects of temperature and concentration on the *m* and *n* ((a) concentration (kg/m^3): ■, 10; □, 15; ●, 20; ○, 25; ◆, 30; (b) temperature (°C): ◆, 20; ○, 22; ●, 25; □, 27; ■, 30).

For a power-type relationship, *m* and *n* varies with the concentration raised to a given power

$$m = m_1 C^{m2} \tag{8}$$

$$n = n_1 C^{n2} \tag{9}$$

and, for an exponential-type relationship the function is exponential:

$$m = m_3 \exp(m_4 C) \tag{10}$$

$$n = n_3 \exp(n_4 C) \tag{11}$$

Variation of $\log m_0$ and A_1 constants in Eq. (6) with concentration can be described by the following equations

$$\log m_0 = (\log m_0)_1 C^{(\log m_0)_2} \tag{12}$$

$$A_1 = A_{11} C^{A_{12}} \tag{13}$$

$$\log m_0 = (\log m_0)_3 \exp((\log m_0)_3 C) \tag{14}$$

$$A_1 = A_{13} \exp(A_{14} C) \tag{15}$$

The effect of temperature and concentration on the m and n could be combined into a single equation for use in process where simultaneous heat and mass transfer takes place. Eqs. (16)–(19) can be obtained by combining the Eqs. (6), (12)–(15)

$$\log m = (\log m_0)_1 C^{(\log m_0)_2} - A_{11} C^{A_{12}} T \tag{16}$$

$$\log m = (\log m_0)_1 C^{(\log m_0)_2} - A_{13} \exp(A_{14} C) T \tag{17}$$

$$\log m = (\log m_0)_3 \exp((\log m_0)_4 C) - A_{11} C^{A_{12}} T \tag{18}$$

$$\log m = (\log m_0)_3 \exp((\log m_0)_4 C) - A_{13} \exp(A_{14} C) T \tag{19}$$

Variation of n_0 and A_2 constants in Eq. (7) with concentration can be described by the following equations

$$n_0 = n_{01} C^{n_{02}} \tag{20}$$

$$A_2 = A_{21} C^{A_{22}} \tag{21}$$

$$n_0 = n_{03} \exp(n_{04} C) \tag{22}$$

$$A_2 = A_{23} \exp(A_{24} C) \tag{23}$$

Eqs. (24)–(27) can be obtained by combining the Eqs. (7), (20)–(23)

$$n = n_{01} C^{n_{02}} + A_{21} C^{A_{22}} T \tag{24}$$

$$n = n_{01} C^{n_{02}} + A_{23} \exp(A_{24} C) T \tag{25}$$

$$n = n_{03} \exp(n_{04} C) + A_{21} C^{A_{22}} T \tag{26}$$

$$n = n_{03} \exp(n_{04} C) + A_{23} \exp(A_{24} C) T \tag{27}$$

$(\log m_0)_1$, $(\log m_0)_2$, $(\log m_0)_3$, $(\log m_0)_4$, A_{11}, A_{12}, A_{13}, A_{14}, n_{01}, n_{02}, n_{03}, n_{04}, A_{21}, A_{22}, A_{23}, A_{24} constants in Eqs. (16)–(19) and Eqs. (24)–(27) were determined by multiple regression analysis of the experimental data in the temperature range 20–30 °C and in the concentration range 10–30 kg/m^3. The results of regression analysis are tabulated in Table 3.

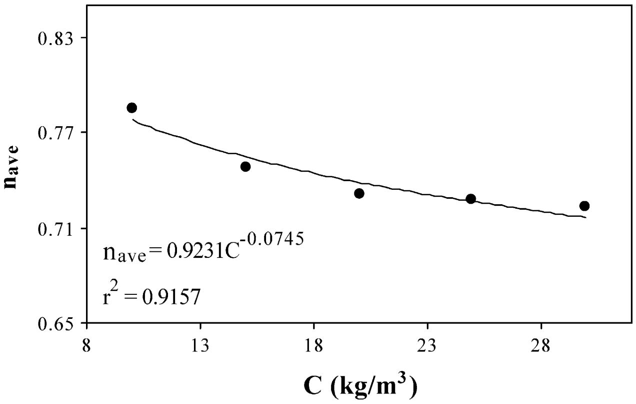


Fig. 3. Relationship of average flow behaviour index and concentration.

Table 3
Values of parameters of the theorical models described by Eqs. (16)–(19) and Eqs. (24)–(27)

Equations	Constants		Equations	Constants	
16	$(\log m_0)_1$	4.935	17	$(\log m_0)_1$	0.1283
	$(\log m_0)_2$	0.0822		$(\log m_0)_2$	0.3314
	A_{11}	0.0257		A_{13}	0.0089
	A_{12}	0.0297		A_{14}	-0.0047
	r^2	0.9300		r^2	0.8438
18	$(\log m_0)_3$	0.37194	19	$(\log m_0)_3$	− 2.376
	$(\log m_0)_4$	− 0.0803		$(\log m_0)_4$	− 0.0072
	A_{11}	0.0130		A_{13}	1.8945
	A_{12}	− 0.1997		A_{14}	− 1.833
	r^2	0.8339		r^2	0.6816
24	n_{o1}	1.717	25	n_{o1}	0.00002
	n_{o2}	− 0.7350		n_{o2}	2.549
	A_{21}	0.0010		A_{23}	0.0029
	A_{22}	0.1986		A_{24}	− 0.0109
	r^2	0.8867		r^2	0.9141
26	n_{o3}	0.0034	27	n_{o3}	0.0059
	n_{o4}	0.0867		n_{o4}	0.0925
	A_{21}	0.0035		A_{23}	0.0028
	A_{22}	− 0.1218		A_{24}	− 0.0098
	r^2	0.9264		r^2	0.9049

$(\log m_0)_1 : (\mathrm{kg/m^3}) - (\log m_0)_2$, $(\log m_0)_2 : [-]$, $A_{11} : (\mathrm{kg/m^3})^{-A_{12}}\,\mathrm{K}^{-1}$, $A_{12} : [-]$, $(\log m_0)_3 : [-]$, $(\log m_0)_4 : (\mathrm{kg/m^3})^{-1}$, $A_{13} : [-]$, $A_{14} : (\mathrm{kg/m^3})^{-1}$; $n_{01} : (\mathrm{kg/m^3})^{-n_{02}}$, $n_{02} : [-]$, $A_{21} : (\mathrm{kg/m^3})^{-A_{22}}\,\mathrm{K}^{-1}$, $A_{22} : [-]$, $A_{23} : \mathrm{K}^{-1}$, $A_{24} : (\mathrm{kg/m^3})^{-1}$, $n_{03} : [-]$, $n_{04} : (\mathrm{kg/m^3})^{-1}$.

The criteria used for model selection was the magnitude of the determination coefficient. From Table 3, it can be seen that the empirical relations that give the best prediction for the temperature and concentration dependence of *m* and *n* are described by the Eqs. (16) and (26). The variation of *m* values calculated using Eq. (16) with temperature and concentration in the temperature range 20–30 °C and in the concentration range 10–30 kg/m^3 is shown in Fig. 4.

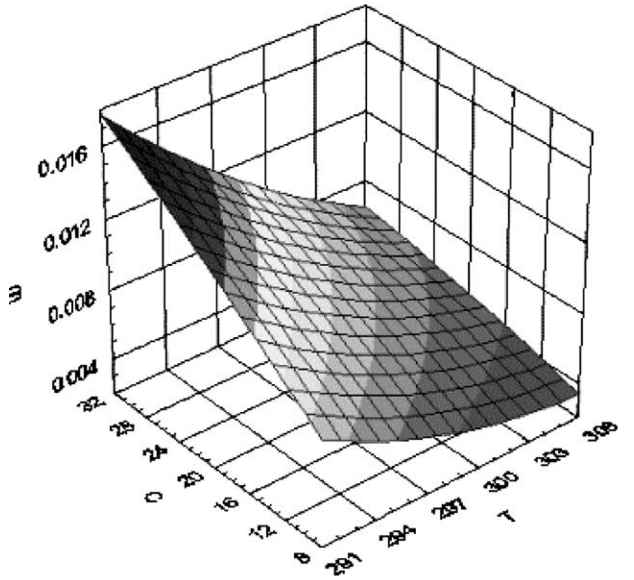


Fig. 4. Variation of *m* values calculated using Eq. (16) with temperature and concentration. *m* (Pa s^n), *T* (K), *C* (kg/m^3).

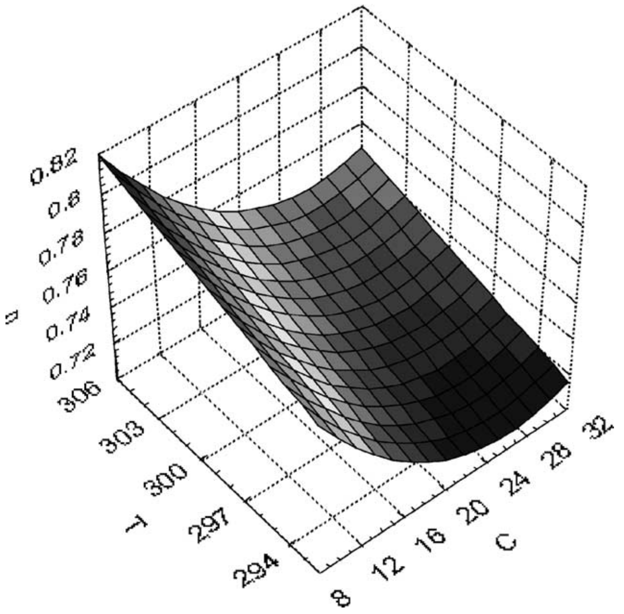


Fig. 5. Variation of *n* values calculated using Eq. (26) with temperature and concentration. *n* (dimensionless), *T* (K), *C* (kg/m^3).

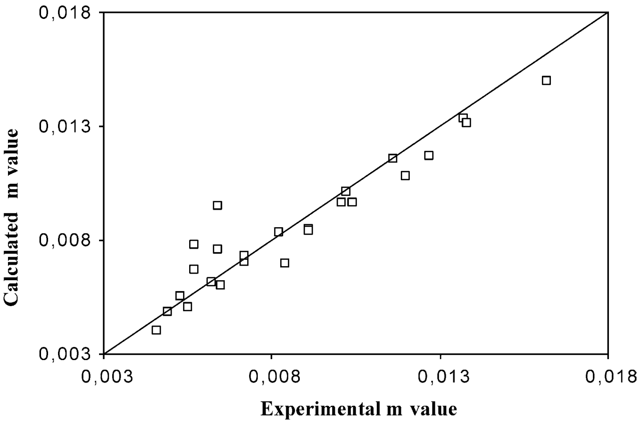


Fig. 6. Comparison of experimental *m* values and m values calculated using Eq. (16).

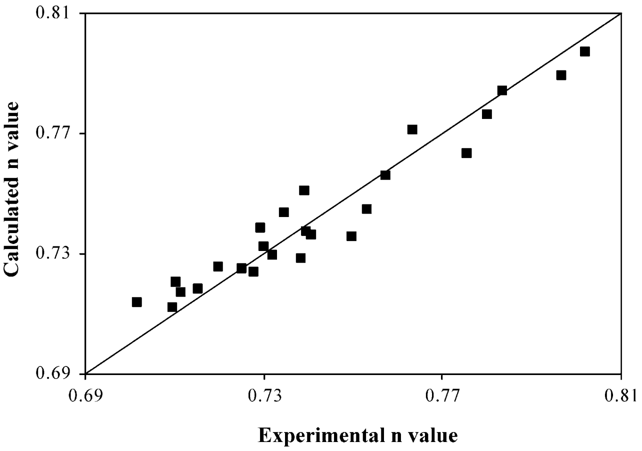


Fig. 7. Comparison of experimental *n* values and *n* values calculated using Eq. (26).

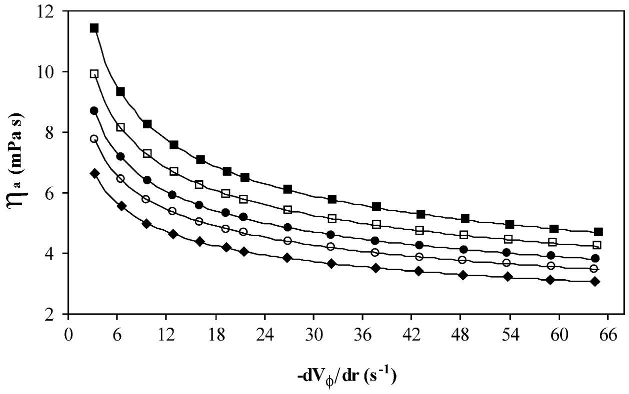


Fig. 8. Apparent viscosity as a function of shear rate (temperature (°C): ■, 20; □, 22; ●, 25; ○, 27; ◆, 30).

The variation of n values calculated using Eq. (26) with temperature and concentration in the range of the concentration of 10–30 kg/m^3 and 20–30 °C temperatures is shown in Fig. 5.

The pooled data for m and n values calculated by the Eqs. (16) and (26) versus experimental values are presented in Figs. 6 and 7 which shows an overall uniform good distribution (as indicated by the r^2 values of 0.9300 and 0.9264, respectively) of data points along the perfect diagonal line.

Eqs. (16) and (26) can be used for the estimate of m and n values at temperature and concentration range studied.

3.4. The combined effect of temperature and concentration on apparent viscosity

For non-Newtonian fluids, it may use the apparent viscosity (η_a) at a specific shear rate instead of the viscosity (Rao, Cooley, & Vitali, 1984). In order to study the effect of temperature on the flow behaviour of CMC solutions, the η_a were calculated at all shear rates for different temperature and concentration using the following equation:

$$\eta_a = \tau_{r\phi}/(-dV_\phi/dr) \tag{28}$$

Fig. 8 shows the relationship of apparent viscosity and shear rate for the concentration of 30 kg/m^3.

As expected, η_a decreases with increase in shear rate, which shows that the flow behaviour of CMC solutions is pseudoplastic. The decrease in η_a can be attributed to the break of macromolecular aggregates. Aggregates are very common in polyelectrolytes derived from polysaccharides in aqueous solution (Almedia & Dias, 1997). As usual, η_a decreases as the temperature at which the viscosity is measured increases. This behaviour is completely reversible due to the interaction of the molecules in solution. This effect is caused by the loss of hydration water around the polymer molecule increasing flexibility of the polymer chain (Casas, Mohedano, & Ochoa, 2000). An Arrhenius type equation was attempted for modelling the variation of the η_a with the temperature in the range of shear rates of 3.24–64.8 s^{-1}. The Arrhenius model is given by (Grigelmo, Ibarz, & Martin, 1999; Rao, Cooley, & Vitali, 1984; Vitali & Rao, 1982)

$$\eta_a = \eta_0 \exp(E_a/RT) \tag{29}$$

where η_a is the apparent viscosity (mPa s); η_0, a parameter that is considered as the viscosity at infinite temperature (mPa s); E_a, activation energy (kJ/mol); R, the molar gas constant (kJ/mol K); T is temperature (K).

Two types of equations could be used to explain the variation of the η_a with the concentration (Rao, Cooley, & Vitali, 1984; Vitali & Rao, 1982).These equations can also be used for η_0. In some cases, the change in viscosity with concentration follows a power-law relationship

$$\eta_0 = \delta(C)^\varepsilon \tag{30}$$

Table 4
The combined effect of temperature and concentration on apparent viscosity of CMC solutions (fitted model Eq. (32))

Shear rate (s^{-1})	$\eta_a = \delta(C)^\varepsilon \exp(E_a/RT)$								
	$\delta \times 10^7$ mPa s (kg/m^3)$^{-\varepsilon}$	ε [−]	E_a (J/mol)	r^2	MPE	MBE	RMSE	EF	χ^2
3.24	1.930	0.6317	38290	0.9795	−0.66447	−0.01416	0.11083	0.9795	0.1198
6.48	5.157	0.5795	35802	0.9708	−0.72600	−0.01392	0.08651	0.9967	0.1028
9.71	9.397	0.5474	34296	0.9631	−0.69404	−0.01331	0.07351	0.9962	0.0965
13.0	14.554	0.5239	33204	0.9557	−0.6414	−0.0127	0.06463	0.9957	0.0931
16.2	20.717	0.5053	32326	0.9489	−0.5833	−0.0122	0.05807	0.9953	0.0909
19.4	27.624	0.4897	31613	0.9421	−0.5252	−0.0117	0.05278	0.9949	0.0894
21.6	32.856	0.4806	31185	0.9376	−0.4866	−0.0114	0.05005	0.9946	0.0886
27.0	47.419	0.4610	30280	0.9270	−0.3951	−0.0107	0.04400	0.9941	0.0871
32.4	46.503	0.4447	29523	0.9166	−4.5329	−0.1627	0.10921	0.9936	0.0860
37.8	84.368	0.4307	28864	0.9065	−0.2308	−0.0097	0.03552	0.9931	0.0852
43.2	106.76	0.4184	28288	0.8966	−0.1566	−0.0093	0.03242	0.9927	0.0845
48.6	131.71	0.4074	27775	0.8870	−2.9118	−0.0950	0.08175	0.9923	0.0840
54.0	159.16	0.3975	27312	0.8776	−0.0221	−0.0085	0.02748	0.9919	0.0835
59.4	189.68	0.3883	26886	0.8683	−2.3242	−0.0732	0.07136	0.9916	0.0831
64.8	223.18	0.3800	26489	0.8591	0.0976	−0.0079	0.02365	0.9912	0.0826

Table 5
The combined effect of temperature and concentration on apparent viscosity of CMC solutions (fitted model Eq. (33))

Shear rate (s^{-1})	$\eta_a = \delta_1 \exp(\varepsilon_1 C)\exp(E_a/RT)$								
	$\delta \times 10^7$ mPa s	ε_1 $(kg/m^3)^{-1}$	E_a (J/mol)	r^2	MPE	MBE	RMSE	EF	χ^2
3.24	5.587	0.0379	38,296	0.9536	1.25553	0.00897	0.08049	0.9732	0.1568
6.48	13.784	0.0354	35,752	0.9771	0.59587	0.00299	0.06169	0.9974	0.0811
9.71	23.897	0.0339	34,216	0.9763	0.31460	0.00056	0.05308	0.9978	0.0569
13.0	35.664	0.0327	33,103	0.9783	0.16129	−0.0007	0.04794	0.9979	0.0458
16.2	49.266	0.0318	32,211	0.9775	0.06851	−0.0016	0.04448	0.9979	0.0310
19.4	64.051	0.0311	31,486	0.9763	0.00931	−0.0021	0.04190	0.9979	0.0366
21.6	75.045	0.0306	31,052	0.9753	−0.0178	−0.0024	0.04030	0.9979	0.0351
27.0	104.81	0.0297	30,135	0.9720	−0.0586	−0.0029	0.03764	0.9978	0.0332
32.4	138.63	0.0289	29,321	0.9684	0.83179	0.00693	0.07328	0.9976	0.0325
37.8	176.95	0.0282	28,707	0.9645	−0.0779	−0.0034	0.03400	0.9974	0.0323
43.2	219.05	0.0276	28,128	0.9602	−0.0716	−0.0035	0.03264	0.9972	0.0326
48.6	264.93	0.0270	27,612	0.9557	0.59527	0.00520	0.06065	0.9970	0.0330
54.0	314.30	0.0265	27,150	0.9510	−0.0438	−0.0037	0.03063	0.9968	0.0335
59.4	368.26	0.0261	26,722	0.9461	0.48603	0.00445	0.05502	0.9966	0.0341
64.8	426.48	0.0256	26,327	0.9411	−0.0038	−0.0037	0.02923	0.9963	0.0346

and, in others the relationship is exponential

$$\eta_0 = \delta_1 \exp(\varepsilon_1 C) \qquad (31)$$

where δ, δ_1, ε and ε_1 are constants.

A single equation combining the effects of temperature and concentration on viscosity of CMC solutions would be useful. Eqs. (32) and (33) were obtained by combining the Eqs. (29)–(31) to obtain the combined effect of temperature and concentration on apparent viscosity. The η_a values were fitted, by multiple linear regression, to the following equations and the overall dependency of apparent viscosity on temperature and concentration was assessed in the terms of the following equations derived by combining the Arrhenius equation, power and exponential relationships

$$\eta_a = \delta C^{\varepsilon} \exp(E_a/RT) \qquad (32)$$

$$\eta_a = \delta_1 \exp(\varepsilon_1 C)\exp(E_a/RT) \qquad (33)$$

The suggested equations will be useful in the prediction of the apparent viscosity at various temperatures between 20 and 30 °C and for concentrations within the range of 5–30 kg/m^3. 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. Tables 4 and 5 show the values of the obtained constants and summary of the statistical analysis.

It should be noted that a decrease in activation energy is always associated with an increase in the shear rate. According to statistical tests, Eq. (33) was more suitable in comparison with Eq. (32). A multiple regression analysis on the apparent viscosity–temperature–concentration data showed that the statistically fitted model of Eq. (33) could be proposed to evaluate the apparent viscosity of CMC solutions for the interval of concentrations and temperatures studied.

The variation of the experimental apparent viscosity and apparent viscosities calculated using Eqs. (32) and (33) with temperature and concentration in the temperature range 20–30 °C and in the concentration range 5–30 kg/m^3 and are shown in Fig. 9.

In all the cases, the effect of concentration on apparent viscosity was more pronounced than the effect of temperature.

Fig. 10 shows the pooled data for apparent viscosity values calculated by the Eqs. (32) and (33) versus

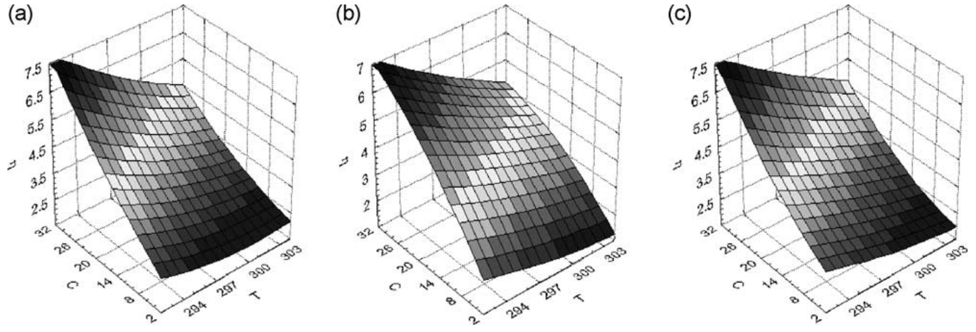


Fig. 9. Variation of apparent viscosity with temperature and concentration ((shear stress:16.2 s^{-1}): (a) experimental apparent viscosity, (b) apparent viscosity calculated using Eq. (32), (c) apparent viscosity calculated using Eq. (33)). η (mPa s), T (K), C (kg/m^3).

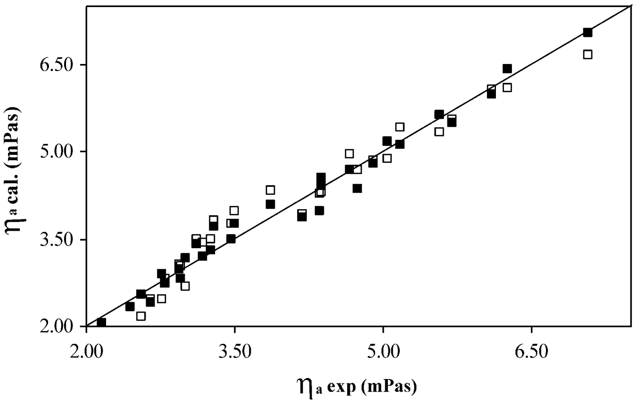


Fig. 10. Comparison of experimental apparent viscosity and calculated apparent viscosity values ((shear stress:16.2 s^{-1}): Eq. (32): □; Eq. (33): ■).

experimental apparent viscosity (r^2 : 0.9489 and 0.9775, respectively).

These results will be a powerful tool in the prediction of the flow behaviour of CMC solutions, allowing the calculation of the pumping requirements and the heat transfer parameters. The data obtained in this study are applicable only in designing equipment for handling of CMC solutions at the temperature range studied.

References

AACC (1983). *Approved methods of the AACC.* St Paul, MN: American Association of Cereal Chemists.

Abdelrahim, K. A., & Ramaswamy, H. S. (1995). High temperature/pressure rheology of carboxymethyl cellulose (CMC). *Food Research International*, *28*(3), 285–290.

Almedia, A. R., & Dias, M. L. (1997). Comparative study of shear degradation of carboxymethylcellulose and poly (ethylene oxides) in aqueous solution. *Polymer Degradation and Stability*, *56*, 331–337.

ASTM (1961). *Tentative methods of testing sodium carboxymethyl cellulose*. ASTM: D1439-61T, pp. 1164–1173.

Barai, B. K., Singhal, R. S., & Kulkarni, P. R. (1997). Optimization of a process for preparing carboxymethyl cellulose from water hyacinth (Eichornai crassipes). *Carbohydrate Polymers*, *32*, 229–231.

Casas, J. A., Mohedano, A. F., & Ochoa, F. G. (2000). Viscosity of guar gum and xanthan/guar gum mixture solutions. *Journal of Science and Food Agriculture*, *80*, 1722–1729.

Charpentier, D., Mocanu, G., Carpov, A., Chapelle, S., Merle, L., & Muller, G. (1997). New hydrophobically modified carboxymethyl cellulose derivatives. *Carbohydrate Polymer*, *33*, 177–186.

Denn, M. M. (1980). *In process fluid mechanics*. Englewoods cliffs, NJ: Prentice-Hall.

Far, B. M (1992). *Karboksimetil selüloz üretimi ve üretimdeki gelismeler*. Master Thesis. Gazi University, Ankara

Fichtali, J., Van De Voort, F. R., & Doyon, G. J. (1993). A rheological model for sodium caseinate. *Journal of Food Engineering*, *19*, 203–211.

Giner, J., Ibarz, A., Garza, S., & Xhian-Quan, S. (1996). Rheology of clarified cherry juices. *Journal of Food Engineering*, *30*, 147–154.

Grigelmo, N. M., Ibarz, A. R., & Martin, O. B. (1999). Rheology of peach dietary fibre suspensions. *Journal of Food Engineering*, *39*, 91–99.

Guerrero, S. N., & Alzamora, S. M. (1998). Effect of pH, temperature and glucose addition on flow behaviour of fruit purees. II. Peach, papaya and mango purees. *Journal of Food Engineering*, *37*, 77–101.

Hangen, P., & Tung, M. A. (1976). Rheograms for power-law fluids using coaxial cylinder viscometers and a template method. *Canadian Institute of Food Science and Technology*, *9*, 98–104.

Heinze, T., & Pfeiffer, K. (1999). Studies on the synthesis and characterization of carboxymethylcellulose. *Die Angewandte Makromolekulare Chmie*, *266*, 37–45.

Ibarz, A., Garvin, A., & Costa, J. (1999). Rheological behaviour of sloe (prunus spinosa) fruit juices. *Journal of Food Engineering*, *27*, 423–430.

Ibarz, A., Gonzalez, C., & Esplugas, S. (1994). Rheology of clarified fruit juices. III. Orange juices. *Journal of Food Engineering*, *21*, 485–494.

Ibarz, A., & Pagan, J. (1987). Rheology of raspberry juices. *Journal of Food Engineering*, *6*, 269–289.

Jinescu, C. V. (1974). The rheology of suspensions. *International Chemical Engineering*, *14*, 397–420.

Khalil, K. E., Ramakrishna, P., Nanjundaswamy, A. M., & Patwardhan, M. V. (1989). Rheological behaviour of clarified banana Juice: effect of temperature and concentration. *Journal of Food Engineering*, *10*, 231–240.

Kirk, R. E., & Othmer, D. F. (1967) (2nd ed) (*Vol. 4*). *Cellulose encylopedia of chemical technology*, New York: Wiley, pp. 593–683.

Mahmoud, M. I., & Fugitt, M. (1996). Rheological properties of a calorically dense nutritional supplement as a function of nitrogen source and dietary fiber. *1996 IFT annual meeting, book of abstracts*, *80A-26*, 183.

Marcotte, M., Taherian, A. R., Trigul, M., & Ramaswamy, H. S. (2001). Evaluation of rheological properties of selected salt enriched foods hydrocolloids. *Journal of Food Engineering*, *48*, 157–167.

Mizrahi, S. (1979). A review of the physicochemical approach to the analysis of the structural viscosity of fluid fruit products. *Journal of Texture Studies*, *10*, 67–82.

Muller, F. L., Pain, J. P., & Villon, P. (1994). On the behaviour of non-Newtonian liquids in collinear ohmic heaters. *Proceedings of the 10th international heat transfer conference. Freezing, melting, internal forces convection and heat exchangers, Brighton, UK*, *4*, 285–290.

Olaru, N., Olaru, L., Stoleriu, A., & Timpu, D. (1998). Carboxymethylcellulose synthesis in organic media containing ethanol and/or acetone. *Journal of Applied Polymer Science*, *67*, 481–486.

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.

Savage, A. B., Young, A. E., & Maasberg, A. T. (1954) Derivatives of cellulose. In: Ott, E. (Ed.), *Cellulose and cellulose derivatives*, New York: Interscience Publishers, Inc., pp. 882–958.

Shoemaker, C. F., Lewis, J. I., & Tamura, M. S. (1987). Instrumentation for rheological measurements of food. *Food Technology*, *41*(3), 80–84.

Steffe, J. F. (1992). *Rheological methods in food process engineering* (2nd ed). East Lansing: Freeman Press.

Toğrul, H., & Arslan, N. (2003). Flow properties of sugar beet pulp cellulose and intrinsic viscosity-molecular weight relationship. *Carbohydrate Polymers*, a in press.

Turian, R. M. (1964). *Thermal phenomena and non-newtonian viscometry*. Ph.D. Thesis. University of Wisconsin, Madison.

Vitali, A. A., & Rao, M. A. (1982). Flow behaviour of guava puree as a function of temperature and concentration. *Journal of Texture Studies*, *13*, 275–289.

Vitali, A. A., Roig, S. M., & Rao, M. A. (1974). Viscosity behaviour of concentrated passion fruit juice. *Confructa*, *19*(5), 201–206.

Waring, M. J., & Parsons, D. (2001). Physico-chemical characterization of carboxymethylated spun cellulose fibres. *Biomaterials*, *22*, 903–912.

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.

Westra, J. G. (1989). Rheology of (carboxymethyl) cellulose with xanthan gum properties. *Macromolecules*, *22*, 367–370.