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Rheological Properties of CMC Dispersions at Low Temperatures

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Summary

Carboxymethylcellulose (CMC) as a typical hydrocolloid has wide application in many foodstuffs formulation, product development and processing, due to its specific rheological properties. This paper deals with three types of CMC dispersions: of extra high (DVEP – substitution degree 0.78–0.89), high (HVEP – substitution degree 0.70–0.94) and low viscosity (LVEP – substitution degree 0.70–0.85), rheological behaviour of which was investigated by varying mass fraction (0.2, 0.5, 1.0, 1.5 and 2.0%) and temperature (20, 10, 5, 0, –3, –5 and –6 °C, i. e. at the lowest temperatures at which it was possible to perform the measurements). The rheological properties of CMC dispersions were adequately described by Ostwald and Reiner's power-law model and power-law parameters (consistency coefficient and flow behaviour index) as well as by applying Arrhenius model. It was found that type of CMC, temperature and particularly concentration significantly influence the rheological behaviour of CMC dispersions.

Keywords: rheological properties, CMC, low temperatures

Introduction

Hydrocolloids are complex carbohydrates which are used to improve consistency and textural characteristics (rheological properties) of liquid, semiliquid and semisolid foodstuffs. Most of them are not metabolized. Their caloric value is quite low, making them useful particularly in the development of diet foods *(1)*. Generally, hydrocolloids do not have direct influence on the taste and flavour of foodstuffs, but at the same time they have significant effect on gel formation, water retention, emulsifying and aroma retention *(2–6)*.

Carboxymethylcellulose (CMC), as a typical hydrocolloid, due to its properties such as solubility in water, low-to-high viscosity in solution, physiological innocuousness, film forming ability, certain degree of adhesivness, good microbiological stability, suspending and »colloidal« characteristics, has got a large number of applications. In the food industry CMC is used as a stabilizer, binder, thickener, suspending and water-retaining agent, in ice-cream and other frozen desserts, pie fillings, fluid and powdered fruit drinks, sauces and creams, cake mixes and slimming and dietary foods.

Rheological properties of CMC aqueous dispersions have been widely investigated by some authors *(7–10)*. In spite of this and previously mentioned practical applications of CMC in some frozen foods, no accessible references (in literature) to its rheological behaviour at low temperatures have been found so far.

In order to expand earlier studies of rheological and thermophysical properties of particular hydrocolloids, their mixtures and model systems at freezing temperatures *(10,11)*, in this paper the autors carried out an investigation the objective of which was to study the effect of the type (extra high-, high-, and low-viscous) and concentration on the rheology of CMC in aqueous dispersions at low temperatures.

Materials and Methods

The rheological properties of three different types of commercial CMC (Guliver-Chemie, Wiener Neudorf, Austria), extra high viscous (DVEP), high viscous (HVEP), and low viscous (LVEP) were investigated. CMC dispersions (0.2, 0.5, 1.0, 1.5 and 2.0%; mass fractions) were prepared by hydrating in distilled water by vigorous hand mixing at 30 °C. The rheological measurements were made after 24 hours in order to release air bubbles. Measurements were performed by means of a rotational viscometer Rheotest 3 (WEB MLV) with coaxial cylinders, carrying out steady-shear stress (τ) and shear rate (D) with shear rate increasing from the lowest value for every system to 1312 s^{-1} (»upwards«), as well as from 1312 s^{-1} (»downwards«) to the lowest shear rate. The measurements were made at various temperatures: 20, 10, 5, 0, –3, –5 and –6 °C. –6 °C was the lowest temperature at which it was possible to perform the measurements.

The Ostwald and Reiner's power-law was applied to calculate rheological parameters, consistency coefficient and flow behaviour index:

$$\tau = k \cdot D^{n} \qquad /1/$$

where: τ = shear stress, k = consistency coefficient, D = = shear rate, n = flow behaviour index.

The influence of CMC mass fraction on apparent viscosity at 1312 s^{-1} was registered by applying the following equation:

$$\mu = a \cdot w^{b} \qquad /2/$$

where: μ = apparent viscosity, w = mass fraction.

Parameters a and b were obtained from regression of logarithm of apparent viscosity (at 1312 s^{-1}) *vs.* logarithm of CMC dispersions concentration.

The influence of temperature on the change of apparent viscosity of CMC dispersions was monitored by applying the Arrhenius model:

$$\mu = A \cdot e^{E_a/RT} \qquad /3/$$

where: A = frequency factor, E_a = activation energy, R = = gas constant.

Slope and intercept of logarithm of regression of apparent viscosity at 1312 s^{-1} *vs.* $1/T$ were applied for A and E_a value calculating.

Results and Discussion

Based on the dependence of the shear stress on the shear rate the type of solutions was determined. From the typical curves of dependence of the shear stress on shear rate (Fig.1) it could be seen that all CMC dispersions had pseudoplastic behaviour.

Consequently, from the results obtained rheological parameters (consistency coefficient and flow behaviour index) have been derived for all samples (CMC types) and all conditions, mass fraction (0.2–2.0%) and temperatures as mentioned in Materials and Methods.

As it could have been expected, under equal conditions, the highest consistency coefficient was determined for extra high viscous CMC (DVEP) dispersions and the lowest for low viscous CMC (LVEP) dispersions, respectively. At the same time the flow behaviour index was inverse.

Temperature lowering resulted in consistency increase in all CMC dispersions. For example, the temperature change from 20 to –3 °C caused three-fold consistency coefficient increase (from 8137.5 mPa s^n to 26833.44 mPa s^n) for the 2.0% CMC (DVEP) dispersion. At the same time temperature decrease resulted in the flow behaviour index decrease (from 0.4846 to 0.3435)

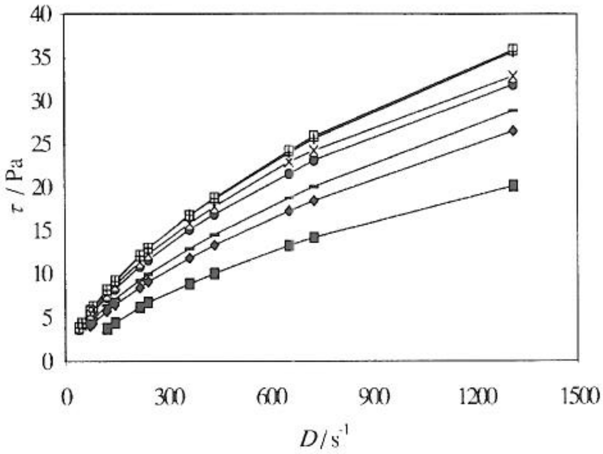

Fig. 1. Shear stress and shear rate relationship of 0.5% (mass fraction) CMC (HVEP) solutions, at various temperatures; ■ 20 °C, ◆ 10 °C, – 5 °C, ● 0 °C, × –3 °C, + –5 °C, □ –6 °C

which indicates that at lower temperature pseudoplastic behaviour was effected more. This phenomenon could be attributed to the orientation of the CMC macromolecules, i.e. to their alignment in the direction of the shearing force *(12,13)*.

The influence of concentration on consistency of CMC dispersions was generaly higher than that of temperature or type of CMC. Namely, the augmentation of mass fraction from 0.2 to 2.0% contributed more to consistency of CMC dispersions increase than the change (lowering) of temperature from 20 to –6 °C. For instance, when the DVEP fraction was increased from 0.2 to 2.0% at 20 °C the consistency coefficient increased about 83 times (from 97.74 mPa s^n to 8137.5 mPa s^n). However, by lowering the temperature from 20 to –6 °C the consistency of the same samples (1.0%) increased only three times (from 1419.20 mPa s^n to 4609.92 mPa s^n). Under equal conditions ($0.2\% \le w \le 2.0\%$) the consistency of HVEP dispersion increased about 51 times (from 64.31 mPa s^n to 3287.0 mPa s^n) while that of LVEP increased about 78 times (from 6.5 mPa s^n to 508.1 mPa s^n).

Table 1. Apparent viscosity (at 1312 s^{-1}) as a function of mass fraction (0.2 – 2.0%) of three types of CMC from 20 to –3 °C

Sample	t/°C	$\frac{100\,a}{\text{mPa s}}$	b	R^2
DVEP	20	58.372	1.266	0.915
	10	79.744	1.312	0.989
	5	85.306	1.272	0.991
	0	91.311	1.240	0.990
	–3	93.260	1.215	0.990
HVEP	20	44.507	1.266	0.953
	10	54.162	1.171	0.981
	5	58.814	1.164	0.983
	0	66.199	1.189	0.984
	–3	69.995	1.190	0.984
LEP	20	40.063	1.159	0.943
	10	53.902	1.242	0.959
	5	63.243	1.301	0.975
	0	74.654	1.307	0.980
	–3	83.576	1.303	0.980

The fact that by using CMC many significant effects could be obtained, such as solutions of various consistency, is very important in different kinds of food development. For example, the types of CMC with HVEP could be successfully applied not only for the products for which high viscosity is required, but also for obtaining some other effects. For instance, by adding the HVEP CMC, in addition to obtaining the particular consistency, a good structure of the product could be obtained as a result of ice crystal growing prevention. This phenomenon is due to the system viscosity increase because of mass transfer decrease and large ice crystal formation, as well as to the CMC hydrophilic properties. On the other hand, the low viscosity CMC (LVEP) has a particular application in production of those foodstufs for which viscosity is not so important (e.g. instant beverages, low-calory food and beverages) as some other effects of CMC such as achieving the particular mouthfeel or prevention of some components sedimentation.

The effect of concentration on apparent viscosity of CMC dispersions at 1312 s^{-1} was monitored by using Eqn. (2). This equation has been, among the others, successfully applied for describing the influence of concentration on rheological properties of xantan gums solutions, as well as for describing the influence of concentration on rheological properties of real systems (e.g. apple and pear juices) (*5,14*). In the Table 1, *a* and *b* parameters and determination coefficient values of that model are shown. As can be seen from the data given in Table 1, apparent viscosity was strongly influenced by CMC dispersion concentration indenpendently of CMC type. The temperature also significantly affects the rheological properties. Namely, by increasing the temperature the consistency of the system decreases. This phenomenon is the result of several factors, i.e. the increase of the distance among the molecules, as well of the changes in the structure and interaction between some constituents. This model is applied to describe the temperature influence on rheological behaviour of some model and real systems. Among others, the influence of temperature (5–45 °C) on rheological properties of xantan gums solutions, as well as the influence of temperature (5–60 °C) on rheological properties of whey proteins has been determined (*5,15*). The data concerning temperature influence on apparent viscosity obtained by means of Arrhenius model are given in Table 2, from which it can be seen that temperature decrease resulted in the apparent viscosity increase in all CMC type solutions (Fig. 2–4).

Table 2. Apparent viscosity (at 1312 s^{-1}) as a function of temperature of solutions of three types of CMC at mass fractions of 0.2 to 2.0%

Sample	w/%	Temperature range/°C	E_a / kJ/mol	A / Pa s	R^2
DVEP	0.2	20 to –5	13.474	$3.73 \cdot 10^{-5}$	0.997
	0.5	20 to –5	11.704	$1.85 \cdot 10^{-4}$	0.993
	1.0	20 to –6	22.314	$4.14 \cdot 10^{-6}$	0.815
	1.5	20 to –5	10.374	$1.63 \cdot 10^{-3}$	0.950
	2.0	20 to –3	5.191	$2.46 \cdot 10^{-2}$	0.960
HVEP	0.2	20 to –5	12.987	$4.64 \cdot 10^{-5}$	0.989
	0.5	20 to –6	19.939	$3.81 \cdot 10^{-6}$	0.941
	1.0	20 to –6	12.225	$2.66 \cdot 10^{-4}$	0.971
	1.5	20 to –5	11.960	$5.79 \cdot 10^{-4}$	0.976
	2.0	20 to –3	10.722	$1.52 \cdot 10^{-3}$	0.909
LVEP	0.2	20 to –5	11.315	$7.99 \cdot 10^{-5}$	0.947
	0.5	20 to –3	19.890	$3.41 \cdot 10^{-6}$	0.958
	1.0	20 to –5	25.187	$8.00 \cdot 10^{-7}$	0.983
	1.5	20 to –3	15.956	$9.57 \cdot 10^{-5}$	0.960
	2.0	20 to –3	9.511	$2.35 \cdot 10^{-3}$	0.946

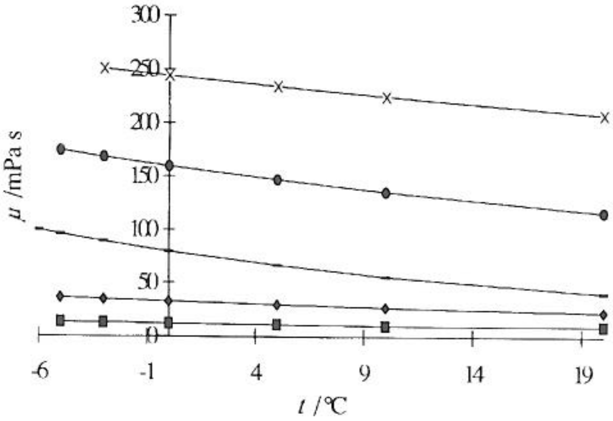

Fig. 2. Dependence of apparent viscosity (at 1312 s^{-1}) of 0.2–2.0% (mass fraction) solutions of CMC (DVEP) on temperature; ■ 0.20%, ♦ 0.50%, – 1.00%, ● 1.50%, × 2.00%

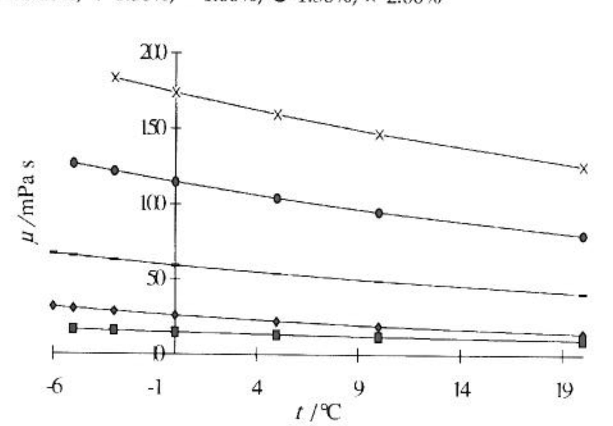

Fig. 3. Dependence of apparent viscosity (at 1312 s^{-1}) of 0.2–2.0% (mass fraction) solutions of CMC (HVEP) on temperature; ■ 0.20%, ♦ 0.50%, – 1.00%, ● 1.50%, × 2.00%

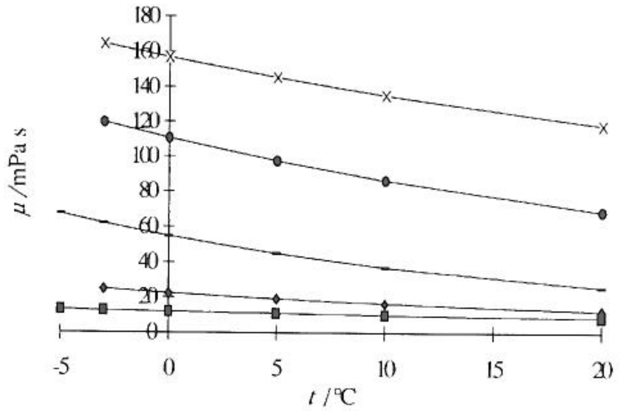

Fig. 4. Dependence of apparent viscosity (at 1312 s^{-1}) of 0.2–2.0% (mass fraction) solutions of CMC (LVEP) on temperature; ■ 0.20%, ♦ 0.50%, – 1.00%, ● 1.50%, × 2.00%

Conclusion

The rheological properties of CMC dispersion were adequately described by power-law parameters (consistency coefficient and flow behaviour index) and Arrhenius model.

All dispersions of three types of commercial CMC (DVEP, HVEP and LVEP) showed pseudoplastic behaviour at all measured temperatures (20, 10, 5, 0, –3, –5, and –6 °C).

Type of CMC, temperature, and particularly concentration, significantly influenced the rheological behaviour of CMC dispersion.

References

1. J. L. Kokini, K. L. Bistany, P. L. Mills, *J. Food Sci. 49* (1984) 1569.
2. J. D. Dziezak, *Food Technol. 45* (1991) 118.
3. J. M. Carr, *Food Technol. 47* (1993) 100.
4. K. L. Krumel, N. Sarkar, *Food Technol. 29* (1975) 36.
5. R. A. Speers, M. A. Tung, *J. Food Sci. 51* (1986) 96.
6. H. M. Bai, J. K. Ahn, Y. H. Yoon, H. U. Kim, *Korean J. Anim. Sci. 20* (1978) 436.
7. Th. Griebel, W.-M. Kulicke, *Getreide, Mehl, Brot, 5* (1992) 154.
8. K. A. Abdelrattim, H. Ramaswamy, G. Doyom, C. Toupin, *Int. J. Food Sci. Technol. 29* (1994) 243.
9. J. I. L. Cottrell, G. Pass, G. O. Phillips, *J. Sci. Food Agric. 31* (1980) 1066.
10. D. Šubarić, V. Piližota, T. Lovrić, *Prehrambeno-tehnol. biotehnol. rev.* 32 (1994) 71.
11. V. Hegedušić, V. Piližota, D. Šubarić, *Prehrambeno-tehnol. biotehnol. rev.* 32 (1994) 67.
12. H. Rosema W.A. Beverloo, *Lebensm. Wiss.-Technol. 7* (1974) 223.
13. A. A. Vitali, M. A. Rao, *J. Texture Stud. 13* (1982) 275.
14. A. Ibarz, M. Vincente, J. Graell, *J. Food Eng. 6* (1987) 257.
15. Q. Tang, P. A. Munro, O. J. McCarthy, *J. Dairy Res. 60* (1993) 349.

Reološka svojstva otopina CMC pri niskim temperaturama

Sažetak

Karboksimetilceluloza (CMC), kao tipičan hidrokoloid, ima raznovrsnu primjenu u proizvodnji mnogih namirnica, zahvaljujući svojim specifičnim reološkim svojstvima.

Predmet ovog istraživanja je mjerenje reoloških svojstava disperznih otopina triju vrsta karboksimetilceluloze, i to: osobito visokoviskozne (»DVEP« – stupanj supstitucije 0,78–0,89), visokoviskozne (»HVEP« – stupanj supstitucije 0,70–0,94) i niskoviskozne (»LVEP« – stupanj supstitucije 0,70–0,85). Mjerenja su provedena pri različitim masenim udjelima (0,2; 0,5; 1,0; 1,5 i 2,0%) i temperaturama (20, 10, 5, 0, –3, –5 i –6 °C, tj. pri najnižim temperaturama pri kojima je bilo moguće provesti mjerenje za pojedini sustav).

Reološka svojstva otopina CMC uspješno su opisana Ostwald-Reinerovim zakonom i odgovarajućim parametrima (koeficijent konzistencije i indeks strujanja), kao i primjenom Arrheniusova modela.

Utvrđeno je da tip karboksimetilceluloze, temperatura i osobito koncentracija značajno utječu na reološka svojstva otopina CMC.