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Quantitative colourimetric assessments of carboximethylcellulose in anionic and anionic-ionic food recipes

C. Jianu, Ileana Cocan, Cristina Rujescu, A. Rinovetz, G. Bujancă, I. Jianu

Banat's University of Agricultural Sciences and Veterinary Medicine, Faculty of Food Processing Technology, 300645-Timişoara, C. Aradului 119, Romania

Abstract

The paper presents a colorimetric ***(500 – 700 nm)*** quantitative method for the determination of carboxymethylcellulose (***CMC***) in the ionic – nonionic foods based on the acid hydrolysis of ***CMC*** and condensation with diphenylamine.

Keywords: carboximethylcellulose, anionic food recipes, nonionic food recipes, food additivation

1. Introduction

Among colloidal additivation (up to ***3%***) accessed in food industry in order to diminish dirt tendency to re-attach (food sanitising) or to increase the deflocculating power, carboximethylcellulose (***CMC***) is of great importance ***[1]***.

Chemically, it is a macromolecular compound made up of units of ***β-D – glucopiranose*** mutually grafted ***β – (1.4) – glycosidic***. Due to the equatorial conformation of the links, the chains have a linear structure with no ***helices***, and with a high ***capacity of associating through hydrogen links*** and of forming ***insoluble crystalline structures***. In order to access it as a ***food additive***, we need to improve the solubility factor through chemical processes (***cellulose gums***).

Solubilising cellulose can be done by etherifying the ***three reactive hydroxyl groups*** of each glucose fragment. In order to get the etherified derivative, first we solubilise the glucose in concentrated alkaline solutions, after which we etherify it heterogeneously under controlled conditions to get the desired substitution degree (***Figure 1***).

The most used ethers (acknowledged from a food point of view) are ***carboximethylcellulose (CMC), methylcellulose (MC), hydroxi-propyl-methyl-cellulose (HPMC)*** together with ***methyl-ethyl-cellulose (MEC)*** or ***hydroxi-propyl-cellulose (HPC) (Table 1)***.

Table 1. Uses of cellulose derivates in food processing [1]

Food products	***Cellulose derivates***						***Coloidaly competences***					
	1	***2***	***3***	***A***	***B***	***C***	***D***	***E***	***F***	***G***	***H***	***I***
Flour products	+		+		+		+		+			
Products from potato	+	+			+		+					+
Meal, fish	+		+	+		+						+
Mayonnaise, dressings	+		+	+	+			+				
Fruit jelly	+			+	+	+						

Corresponding author: *e-mail address*: calin.jianu@gmail.com

Fruit juice	+			+								
Beer	+	+								+	+	
Wine	+	+								+	+	
Ice - cream	+			+	+			+				
Dietetical products	+	+	+		+							

1–CMC natrium salt; ***2***–methyl cellulose; ***3***–HPMC; ***A***–thickening agent; ***B***–water-linking capacity; ***C***–low-temperature jellifying; ***D***–high temperature jellifying; ***E***–emulgator and emulsion stabiliser; ***F***–suspension agent; ***G***–surface-active agent; ***H***–adsorbent; ***I***–film-maker.

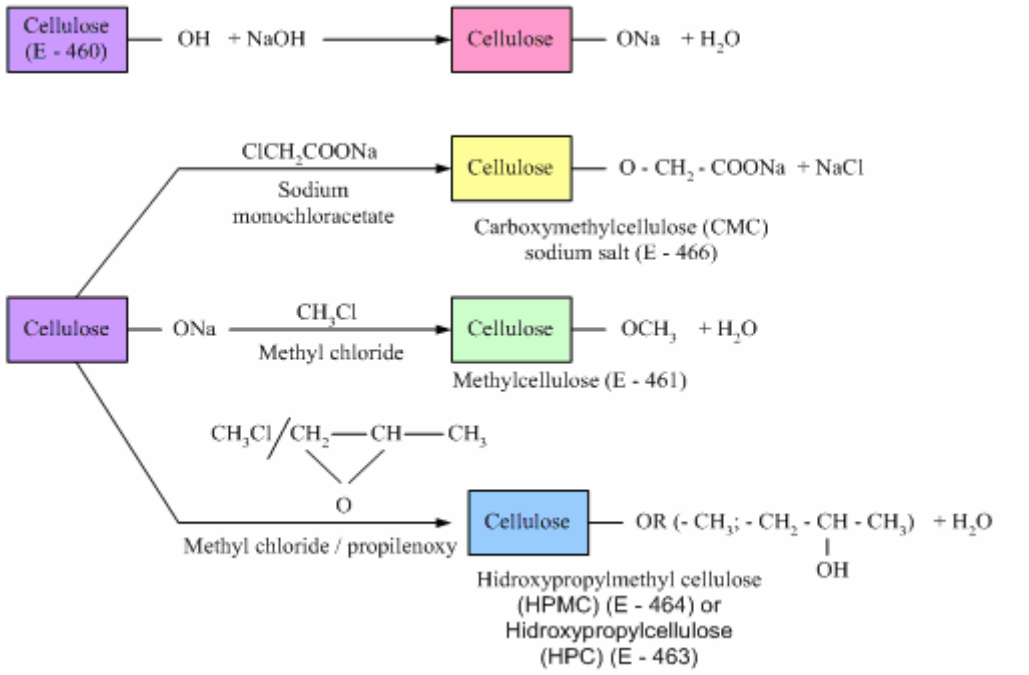


Figure 1. Ways of derivatising cellulose chemically [1]

The most important ether derivative of cellulose from a food point of view is ***CMC*** natrium salt, which differs from an assortment point of view by molecular volume and substitution degree (etherifying). ***CMC*** dissolves easily in water, forming viscous solutions whose concentrations are below ***1%***, and whose behaviour is pseudo-plastic when flowing (in the case of low shearing rates it behaves Newtonian-like).

Literature signals synergic effects between ***CMC,*** guar gum and locust gum, with an increase of viscosity. ***CMC*** forms gels in the presence of trivalent metallic cations (aluminium sulphate, basic aluminium acetate, ferric phosphate). By using kellation agents (citrate or malate), ***pH*** and temperature change, we can control the jellifying rate and gel texture.

The main competences of the ***CMC*** confer it diverse functionalities (linking agent, stabiliser of compounds or syneresis prevention).

As a stabilising agent, ***CMC*** plays the role of preventing protein (soy or milk) precipitation for ***pH*** values close to the isoelectric point and it controls ice crystal formation during ice-cream processing. Due to its water solubility and to the high capacity of grafting water, ***CMC*** is recommended in diet food products as a dissolvent, conferring them a pleasant texture, consistency, and melting characteristics.

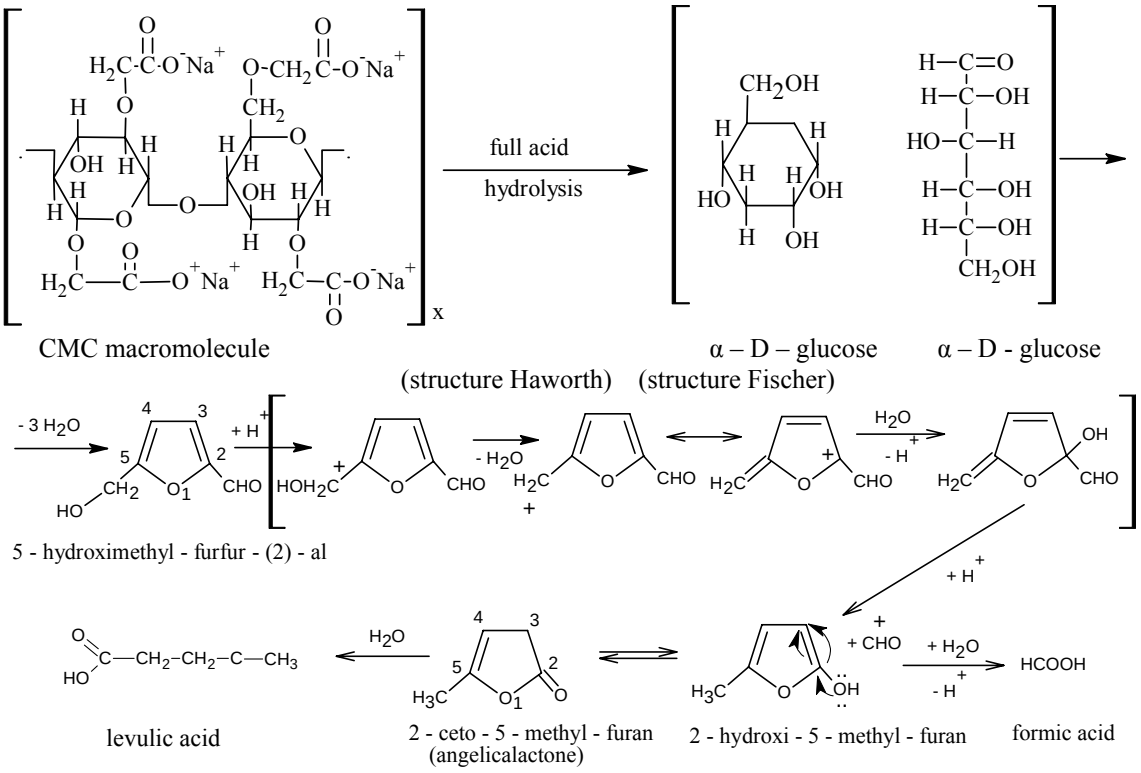
It is often used in mixture with other ***gums*** (gelatine, pectin, or locust gum). The quantitative assessment method adapted and presented in this paper is based on

colourimetry within the range ***490-680 nm*** of colour compounds obtained by condensing di-phenyl-amine with 5-hydroxi-methyl-furfurol obtained through acid hydrolysis of cellulose derivatives.

Pechmann and Ilk [1885] [2, 3] studied the reaction of fructose with di-phenyl-amine in a concentrated chlorhydric environment with the formation of a blue combination. Later, the reaction was generalised in the case of pentose, hexose, di-, oligo-, and poly-sugars ***[4-10],*** of uronic acids ***[11],*** of nucleic acids ***[12, 13]***, etc. For hydrolysis, they recommend chlorhydric, sulphuric, or perchloric acids in concentrations of ***70%***.

For the condensation phase, we can access a solution of di-phenyl-amine ***0.2-10%*** in ethanol – sulphuric acid, ethanol – chlorhydric acid, acetic acid – chlorhydric acid, acetic acid – sulphuric acid or ethanol – acetic acid – sulphuric acid, etc., and as an organic phase, n – butanol, alcohol n – amylic, isoamylic and chloroform.

Quantitative colourimetric assessment of ***CMC*** was the main concern of many researchers ***[14 – 18]***. In all the variants studied and suggested, they appealed to the acid hydrolysis of the product, followed by condensation with antrone ***[14]***, when they obtained a di-benzantrone derivative with absorption over the range ***620-630 nm***, with ***2, 7*** – di-hydroxi-naphtaline ***[15, 18]***, when they got a derivative of the ***2, 7, 2', 7'*** – tetra-hydroxi – di-naphtyl – ***(1)*** – methane with absorption within the range ***530-550 nm,*** or with phenol ***[16]*** resulting in a condensation product with maximum characteristic absorption at ***490 nm***.



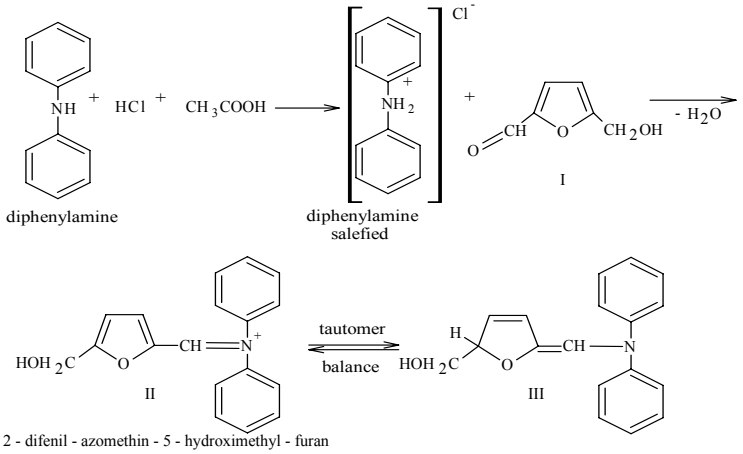


Figure 2. Diagram of the exhaustive acid CMC hydrolysis and diphenylamine condensing mechanism

In the present paper, we have made an option for determining quantitatively ***CMC*** in anionic and non-ionic food recipes to avoid partial hydrolysis of the cellulose derivative without going further than phase ***(I) (Figure 2)***.

2. Experimental part

a. Materials. Reactants

- Re-constituted standard food recipes with anionic and anionic – non-ionic nutritive principles (in the Laboratory of Food Additive Technologies);
- Carboximethylcellulose ***(Merck)***;
- Diphenylamine ***99% (CAS 122-39-4) (Sigma Aldrich)***;
- Different solvents ***(Sigma Aldrich)***.

b. Equipment

- Hydrolysis installation with efficient mechanical stirring, ascending refrigeration thermostat, dripping funnel;
- Colourimeter ***(Cole Parmer) (400 – 600 nm)***;
- ***FT-IR (Büchler)***;
- Qualitative and preparative thin-layer chromatography ***(Camag)***;
- Open-column chromatography ***(Quikfit)***.

Working method

Determining CMC natrium salt by exhaustive acid hydrolysis and condensation with di-phenyl-amine

Preparation of the standard natrium salt CMC solution

In a ***Berzelius*** glass of ***400 mL*** we introduce ***180 – 200 mL*** distilled water. We heat up to ***80°C*** under continuous and efficient stir when we introduce gradually ***4g CMC*** (analytic precision). We continue heating and stirring for about ***20 min*** at the same temperature, then the colloidal solution is put to rest for ***2 hours***, after which it is stirred again for ***20 min*** without heating and is transferred quantitatively into a graded balloon of ***1000 mL*** completing the volume up to the sign. From the solution we can get controlled dilutions within the range ***10 – 100 γ/mL***.

Working way. Drawing the sampling curve and determining CMC proper

We weigh with analytic precision ***0.5 g*** of anionic and/or anionic – non-anionic food recipe in a ***Berzelius*** glass of ***50 mL***, we dissolve in distilled water and later on we transfer into a graded balloon of ***250 mL***; ***3 mL*** of this solution is dropped together with ***6 mL*** of dyphenylamine in the testing tube. We then regulate in the thermostat coat for ***30 min***, at a recycling environmental temperature of ***108 + 0.02°C***. We then cool

suddenly the testing tube and then absorbance at ***580 and 640 nm***.

Graphically, absorbance depending on concentration results in the linearity range of the law ***Lambert – Beer (0 – 5 γ/mL) (Figure 3)***.

In parallel, we prepare a control sample using, instead of the standard ***CMC*** solution, distilled water. Transmission of the sample control should not be below ***90%*** otherwise the diphenylamine is not proper. If necessary, one should also take into account the possible dilutions over the determination period.

The alcoholic solution of diphenylamine will be prepared at the time of the determination, and for no more than four consecutive samples (***0.375 g*** diphenylamine p.a. are dissolved in ***15 mL*** of glacial acetic acid and ***9 mL*** of concentrated chlorhydric acid).

The contents in ***CMC*** of the sample to be assessed can be quantified with the formula:

$$CMC = \frac{A \cdot 1000}{A_{1cm}^{1\%} \cdot a \cdot d}(\%)$$

where:

- A - Sample absorbance;
- $A_{1cm}^{1\%}$ - Molar extinction coefficient ***(g/l · cm)***;
- a - Analyse food recipe amount ***(g/l)***;
- d - Absorbent layer thickness ***(cm)***.

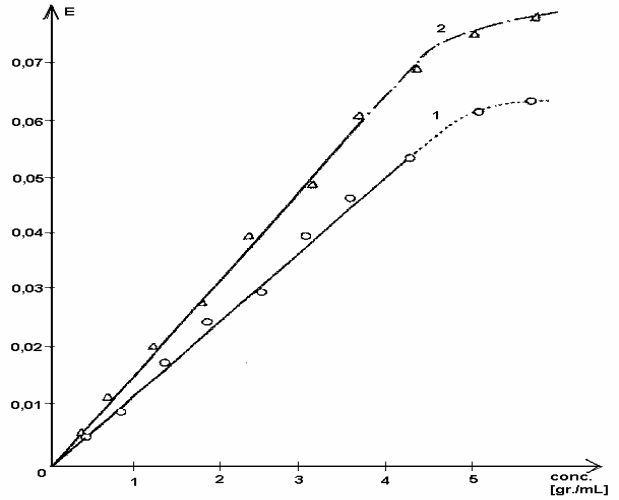


Figure 3. Carboximethylcellulose calibration curve: 1 – for maximum M_1 ; 2 – for maximum M_2

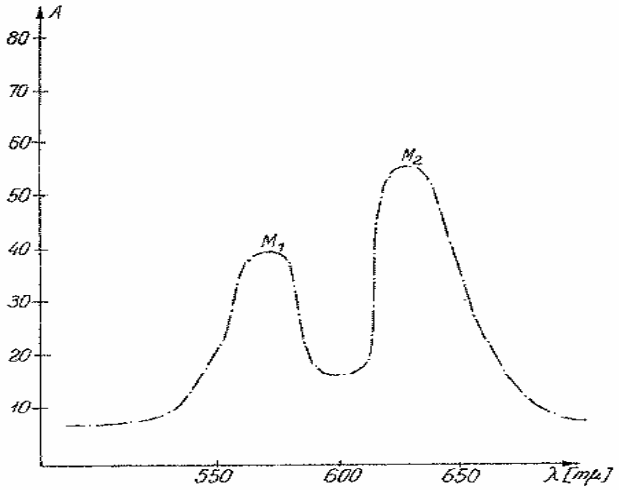


Figure 4. Absorption curve of the condensation compound 5–hydroxi-methyl-furfurol with diphenylamine: M_1 – maximum absorption at 580 nm; M_2 – maximum absorption at 640 nm

3. Results and discussion

Food recipes reconstituted on a classical nutritional structure into an apricot jelly were additivated under monitoring with ***anionic (a)*** superficialactive compounds [sodium lauril sulphate ***(E - 487)***] and ***anionic (b)*** [sodium cetylsulphate ***(E – 487*)***] or ***anionic (a) – non-ionic*** [polysorbates ***(E – 432/436)***]. Salified carboximethylcellulose in the processed recipe was supplementarily controlled ***(Table 2)***.

Table 2. Results of quantitative determination of salified carboximethylcellulose in anionic, anionic – non-ionic food recipes

No.	Nature of additivated food recipe	CMC		Final CMC (%)	Final theoretical CMC (%)	Error (%)	Average relative error (%)	Reproducibility of the method (%)
		determined (%)	additivated (%)					
0	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*
1		3,17	1,84	5,09	5,01	+ 1,59		-
2		3,21	1,42	4,69	4,63	+ 1,22		-
3		3,50	2,08	5,64	5,58	+ 1,08		-
4		2,95	1,75	4,65	4,70	- 1,07		-
5	anionic (a)	3,10	-	3,108*	3,10	+ 0,23	+ 0,864	+ 0,23
6	- nonionic	3,40	-	3,412*	3,40	+ 0,355		+ 0,355
7		3,15	-	3,162*	3,15	+ 0,381		+ 0,381
8		3,60	1,40	4,96		- 0,805		-
9		3,40	1,92	5,40	5,32	+ 1,50		-
10		3,25	2,5	5,70	5,65	+ 0,85		-
11		3,19	1,83	5,00	5,02	- 0,397		-
12		2,88	1,51	4,35	4,39	- 0,92		-
13	anionic (a)	3,08	2,4	5,45	5,48	- 0,55	- 0,347	-
14		3,80	-	3,815*	3,80	+ 0,395		+ 0,395
15		3,45	-	3,441*	3,45	- 0,263		- 0,263
16		3.88	-	3,870	3,88	- 0,258		-
17		3,75	-	3,738	3,75	- 0,322		-
18	anionic (b)	3,24	1,18	4,50	4,42	+ 0,81	- 0,310	-
19		3,35	1,24	4,52	4,59	- 1,55		-
20		3,54	1,35	4,83	4,89	- 1,24		

The quantum of ***CMC*** present and additivated in the apricot jelly was assessed directly with no previous isolation of the cellulose derivative in the product. A possible error in the system was removed by comparing with non-additivated control samples.

Analysing experimental data shows that the balance of theoretical and practical (determined) global material is to be found with an acceptable error ***(- 1.5 ÷ +1.5)***; the method reproducibility is also encouraging ***(- 0.3 ÷ + 0.35).***

4. Conclusions

The method we have described here, rapid and efficient, ensures error results within the range ***±1%***, when recommended analytic conditions are observed.

Determination is not hindered by the presence of other anionic or non-ionic superficialactive substances accidentally or purposely added, though some of them hydrolyse in acid environments in warm conditions (sulphated fatty alcohols, soaps, etc.). Method reproducibility is ± ***0.341%***. We recommend expansion of research to other nutritional systems with the

possibility of later extrapolating and generalising.

Acknowledgment

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