Sudan University ofScience and Technology

College of Graduate Studies

Characterization ofthe Commercial Ice-cream Stabilizer E466 Sodium Carboxymethyl Cellulose

تشخيص مثبت الآيسكريم التجاري E466

صوديوم كاربوكسي ميثيل سيليلوز

A Dissertation Submitted inpartial Fulfillment of theRequirements of the Degree ofM.Scin Chemistry

By

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Dedication

I dedicate this Research to:

MY supervisor **Dr.Kamal Mohammed Saeed**

MY Mother

MY father

ACKNOWLEDGMENT

First of all I would like to thank ALMIGTY ALLAH for giving me patience and help to complete this work

I would not have been possible to write this thesis without and support of the kind people around me, to only some of whom it is possible to give particular mention here.

Above all, I would like to gratefully and sincerely thank Dr. **Kamal Mohammed Saeed** for his guidance, understanding, patience and encouragement

Through all the study.

Abstract

This study focuses on determine of the percent of carboxymethyl cellulose in ice-cream stabilizer which has been used under the number E466 it was determined to be 98.92%. First the percent of sodium chloride determined by Volhard method it was found to be 0.48% then freeflycolate were determined by U.V spectroscopic method the percent was found to be 0.59%. Finally the degree of substitution Ds were determined gravimetrically it was found 0.2. FT-IR spectroscopy also were used to indicated found of carboxymethy species.

مستخلص البحث

هذه الدراسة تركز على تقدير النسبة المئوية لصوديوم كاربوكسي ميثيل سليلوز الذي يستخدم كمثبت في صناعة الايسكريم برقم تجاري 466. أولاً تم تقدير النسبة المئوية لكلوريد الصوديوم باستخدام طريقة فولهارد والتي وجدت 0.48% ثم قدرت نسبة الجلايكوليت الحر باستخدام مطيافية الاشعة المرئية فوق البنفسجية حيث وجدت 0.59%.أخيراً تم تقدير درجة الاستبدال وزنياً حيث وجدت0.2استخدمت مطيافية الاشعة تحت الحمراء للتأكد من وجود مجموعة كاربوكسي مثيل.

Table of content

List of Tables

List of Figures

List of Abbreviations

Term	Page No
CMC	Carboxyl methyl cellulose
LBG	Locust bean gum
WAXS	Wide angle X-ray scattering
DMSO	Dimethyl sufoxide
DMF	Dimethyl formaide
MCAA	Monochloro acetic acid
DS	Degree of substitution
DP	Degree of polymerization
JECFA	Joint FAO/WHO Expert Committee on Food Additives

Chapter one

Introduction

Introduction

1.0General Introduction

Ice cream and related products are generally classified as frozen desserts whichinclude ice cream, frozen custard, frozen confectionaries, ice milk, ice lollies, and sherbetsetc., which are popular among all age group of people. Ice cream is a frozen dairyproduct made by freezing a mix with agitation to incorporate air and ensure uniformity ofconsistency. The complex physical structure of ice cream presents achallenge for food chemists. Simply stated, overall goal of designing the ice cream is toincorporate several different insolubles (air bubbles, ice crystals and fat globules) into anaqueous phase in the smallest sizes and in the greatest numbers possible.

The basic role of a stabilizer is to reduce the amount of free water in the ice creammix by binding it as “water of hydration”, or by immobilizing it within a gel structure.Also it is the ability of small percentage of stabilizer to absorb and hold large amounts ofbound water, which produces good body, smooth texture, slow melt down and heat shockin theresultant product.[Keeney, 1983]

Stabilizers maintain homogeneity and control ice crystal growth during thefreezing/aeration process. During storage, stabilizers play crucial role in resistingstructural changes during “heat shock” (the inevitable temperature during storage anddistribution that creates ice crystal growth and other types of deterioration, leading tostructural changes). During serving and consumption, stabilizers contribute to uniformmeltdown, mouth feel and texture of ice cream. A stabilized ice cream is one that

resistsor retards structural changes in a dynamic environment.(Goff, 1997)

1.1 Formulation of different stabilizer

In ice cream manufacturing, it is always difficult to get all the properties of icecream using a single stabilizer. Today dairy/food technologists have found a newtechnique of blending these stabilizers in different proportions to get excellent propertiesin ice cream.

Most ice cream stabilizers based on polysaccharides influence the rheologicalproperties of the continuous phase. Some stabilizers form a complex with ice creamconstituents, example, carrageenan complexes with casein and prevents whey separationduring mixing. However, when used alone, stabilizers including locust bean gum (LBG),guar gum, carboxymethyl cellulose (CMC) and xanthan gum promote whey separation,due to their tendency to precipitate proteins during heating at neutral pH. Ice creamstabilized with locust bean gum and carrageenan contains significantly smaller icecrystals than ice cream made under identical conditions without stabilizers.[Arbuckl, 1986]

Though alike in many ways, these stabilizers also have many differences withrespect to their property and compatibility. Knowing the characteristics of each allowsproduct designers to incorporate the correct ingredient or ingredient blend in a particularapplication. The choices require consideration of the entire product spectrum frommixing and processing, through finished product attributes, storage and end use.

1.1.1 Gelatin

A high molecular weight polypeptide, gelatin consists of chains of 300 to 4,000amino acids (primarily glycine and proline/hydroxyproline). It is

derived from animalcollagen, mainly pork or beef, but other sources are available, most notably fish. Boilinghydrolyzes the collagen, and converts it into gelatin. Two processes are used, an acidprocess gives type A gelatin and an alkaline process gives type B gelatin. Their propertiesare similar, but type A can negatively interact with other anionic polymers, such ascarrageenan. A thermo reversible gel starts to form when a hot gelatin solution is cooledto below 30º to 35 ºC. At refrigeration temperatures (5ºC), gelatin take 5 to 8 hours toreach maximum gel strength (measured in Bloom). Because the gels dissolve at lowtemperature, they “melt in the mouth” with good flavor release. Levels for a 250 Bloomgelatin are between 0.25% and 0.50% of the mix.

In ice cream industry gelatin forms a gel in the mix as well as during ageing,preventing large ice crystals formation during freezing.[Rawford, 1981, Pyen, 1838, Young, 1986]

1.1.2 Guar Gum

Derived from guar (*Cyamopsistetragonolobus*) seeds, this long, rigid, linearmolecule of beta-1,4-D-galactomannans with alpha 1,6-linked D-galactose has amolecular weight of approximately 1,000,000, giving it a high viscosity in solution. Guargum is an economical thickener and stabilizer. It hydrates fairly rapidly in cold water togive highly viscous pseudoplastic solutions of generally greater low shear viscosity whencompared with other hydrocolloids and much greater than that of locust bean gum. Highconcentrations (~ 1%) are very pseudo plastic but lower concentrations (~0.3%) are farless so. Guar gum is more soluble than locust bean gum and a better emulsifier as it hasmore galactose branch points. Unlike locust bean gum, it does not form gels but doesshow good stability to freeze-thaw cycles. Guar gum shows high low shear viscosity butis strongly shear thinning in nature. Being non ionic, it

is not affected by ionic strength orpH but will degrade at pH extremes at temperature (*e.g.* pH 3 at 50°C). It shows viscositysynergy with xanthan gum. Levels used are up to 0.20%, and depend on the usage levelof other added gums. [Adinugraha, 2005]

Today guar gum is widely used as ice cream stabilizer. Guar is preferred for itsrelatively low cost and the body it contributes to the product. It hydrates well in coldwater, and often used in combination with carrageenan and locust bean gum to impartexcellent properties to ice cream.

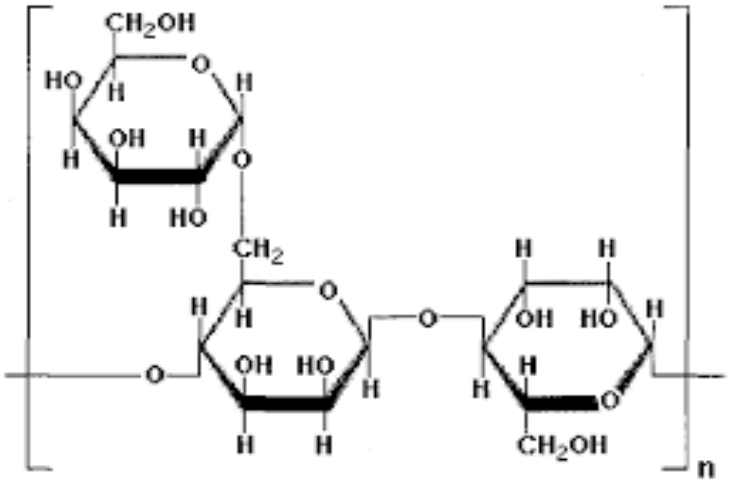


Fig (1.1): Chemical Structure of Guar Gum

1.1.3 Locust Bean Gum

Also called carob gum, as it is derived from carob *(Ceratoniasiliqua*) seeds.Locust bean gum (LBG) has an irregularly shaped molecule with branched beta-1,4-Dgalactomannanunits. This neutral polymer is only slightly soluble in cold water andrequires heat to achieve full hydration and maximum viscosity. LBG does not form a gel,and creates a less gummy texture than guar. It requires heating to 170°F for fullhydration, usually achieved during pasteurization. LBG is inert to acid and calcium.Locust bean gum enhances aeration, and imparts good body to ice cream. Usedalone, it can cause whey-off during processing, so it is

usually used in combination withcarrageenan and guar gum. LBG can act synergistically with kappa-carrageenan andxanthan gum. Usage levels are similar to guar, again depending on which other gums areused in conjunction with it.[Tomas, 2002]

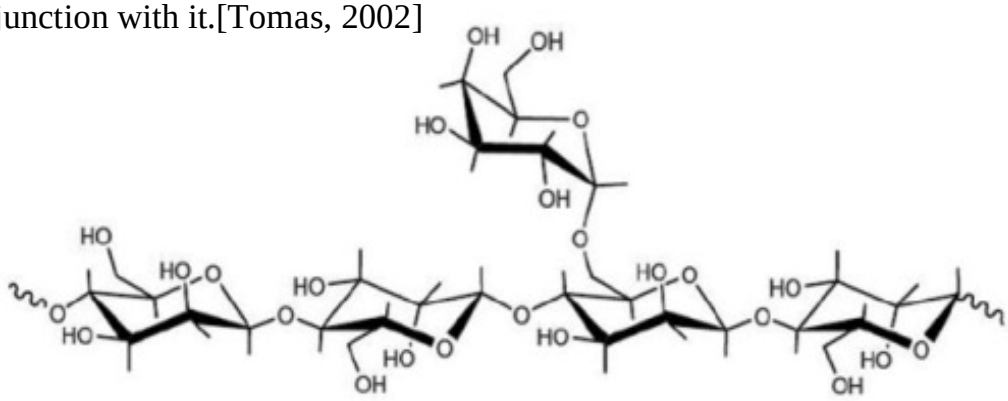


Fig (1.2): Chemical Structure of Locust Bean Gum

1.1.4 Carrageenan

Extracted from Irish moss and other species of red seaweed of the classrhodophyceae, carrageenan is a sulfated linear polysaccharide, which reacts with caseinby forming ionic linkages between sulfate groups and charged amino acids.

Carrageenan is available in several types, the most common of which are kappa,iota and lambda. For low fat and soft serve ice cream compositions, kappa often is usedfor its gel forming functionality and its reactivity with casein, which prevents wheyseparation. It's mandatory to add carrageenan if an aging step exists in the manufacturingprocess. A kappa-iota blend is sometimes preferred, to keep kappa from forming a brittlegel. Lambda blends can be used for ice creams with sufficient fat to stabilize withoutgelling. Kappa and iota solutions require heating for proper hydration. Carrageenan levelscan be used up to 0.05% of the blend.[O'sullivan, 1997]

1.1.5 Alginates

Alginates add a type of body and texture to ice cream that other gums don't easilyduplicate. Extracted from ocean kelp, this natural gum dissolves best at 155° to 160°F.Combined with sodium or phosphate salts, it forms gels at levels from 0.18% to 0.25%.Because it binds calcium, it will reduce the amount of free calcium in the mix.Precipitation of sodium alginate will occur at high calcium levels, making it difficult tohydrate without adding sequesterant.

1.1.6 Xanthan Gum

A product of bacterial fermentation, this giant glucomannan polymer (2 milliondaltons) makes an excellent emulsion/stabilizer because its suspending properties keepemulsions dispersed. It's a popular ingredient in low fat compositions.It can be dispersed by blending with skim milk, corn syrups or nonfat milk solids.Xanthan is cold water soluble, hydrates quickly once dispersed and provides waterbinding. It is always used in combination with other gums. It is synergistic with locustbean gum, which reduces the levels of locust bean gum and guar required. Xanthan gumis heat and pH resistant and also has a cleaner flavor when compared to other gums. Itpossesses pseudoplastic properties and exhibit shear thinning, a useful property forpumping and extrusion in soft serve ice creams. Overuse can cause excessive gelation, anoverly viscous mix, and a chewy ice cream. Usage levels range from 0.015 to 0.040%.However, its cost limits its usage.

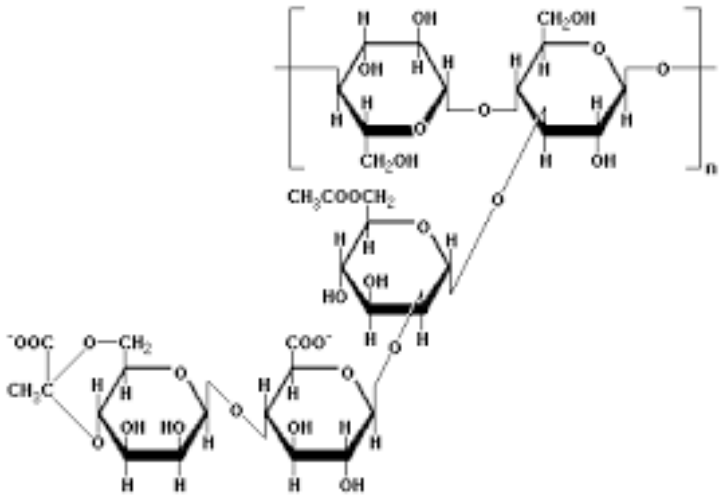


Fig (1.3): Chemical Structure of Xanthan Gum

1.1.7 Carboxymethyl Cellulose

1.1.7.1Cellulose Structure and its source

The chemical formaula of Cellulose was first determined in 1838 by the French chemist AnselmePayen , who isolated it from plant matter [Rawford, 1981, Pyen, 1838, Young, 1986]

Cellulose is a linear and high molecular weight polymers as well as natural renewable and biodegradable material. Due to the hydrogen bonds associated with structure of molecular cellulose, it is neither melted nor dissolved readily in common solvents, [Adinugraha, 2005] but its water soluble usually occurs in the cell wall of plants, it is generally distributed with other substances such as lignin and hemicellulose, which makes it difficult to find in pure form plants contain on a dry basis between 40-55% cellulose, 15-35%lignin and 25-40% hemicelluloses.[Tomas, 2002]

There are two inter convertible polymorphs of cellulose known as cellulose(I) and cellulose (II) X ray crystallography studies of the different cellulose types have showed that cellulose(I) has two chains

that lie parallel to one another in the unit cell. Cellulose(II) has the direction of the chains in the unit cell in an anti parallel orientation.

Cellulose (Fig1.4) can be regarded as a semi-flexible linear chain of 1-4-linked B-D glucopyranose units with a high degree of polymerization(DP) in native fibers (up to 6×10^3 in cotton linters[O'sullivan, 1997]. This is drastically lowered by processing the native fibers of wood pulp.

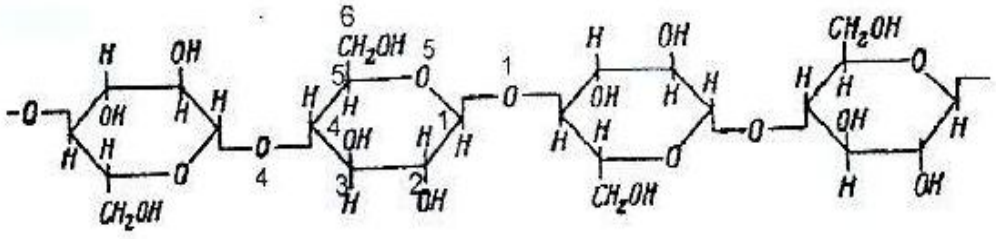


Fig (1.4): The chemical constitution of cellulose

There are three molecular levels of cellulose

The molecular level

In this level cellulose is treated as single macro-molecule and the concepts are considered: chemical constitution molecular mass distribution.

The super molecular level

In level 2, cellulose molecules interact with other cellulose chains in the form of packing to form larger structures, the concepts are of importance: aggregation of the molecular chain to form elementary crystals and fibers.

The morphological level:

The existence of distinct cell wall layers in native cellulose fibers or in the skin core structures in man-made cellulosic fibers.[M.Marx, 1969]

Cellulose has many uses as emulsifier, stabilizer, dispersing agent, thickener, Kraft' Parmesan cheese to prevent caking inside the tube. In

the laboratory cellulose is used as stationary phase for thin layer chromatography and powder cellulose are used as inactive fillers in tablets. Some cellulose derivative material such as methylcellulose and carboxymethylcellulose , are used as water-soluble adhesives and binders as well as constituent of wallpaper paste.[Krassig, 1996]

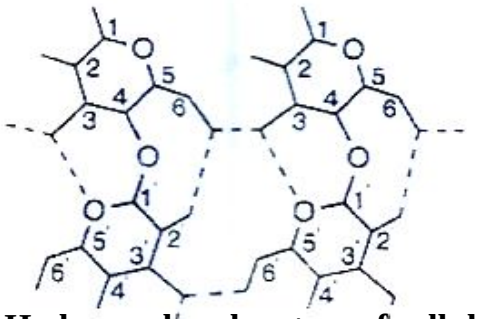
Cellulose is found in plant as micro-fibrils (2-20 nm DIAMETER AND 100-4000 nm long) these form the strong structure of the cell walls. Cellulose is mostly prepared from wood pulp. It isalso produced in highly hydrated form by some bacteria (for example, actetobateraxylinum). The important natural source of cellulose is cotton; it is composed of 91% pure of cellulose, flax, straw, wood , mesquite (40%) and calotropis (42%). [Caoetal, 2009]

1.1.7.2 Hydrogen Bonding

Three hydroxyl groups are available for reaction in each repeating unit ofcellulose, the structure of cellulose being largely affected by hydrogen bonds and vander Waals forces. Hydrogen bonding within neighboring cellulose chains may act todetermine the straightness of the chain, and impart improvedmechanical properties and thermal stability to the cellulose fibers. Inter-chainhydrogen bonds might introduce order or disorder into the system depending on theirregularity. So, understanding hydrogen bonding within the Iαand Iβ structures is important as it governs the stability and properties of thesepolymorphs and of cellulose itself. With the hydroxyl groupsbeing equatorial to the cellulose ring plane, intra- and inter chain hydrogen bonding ismost prevalent within the (110) plane in the triclinic structure and within the (200)plane in the monoclinic structure, hence the name “hydrogen-bonded” plane.On the other hand, intra-chain hydrogen bonding is dominated by strongO3-H⋯O5 bonds, As shown in (Fig1.5).

Inter-chain hydrogen bonding within the other planes (010), (100) in thetriclinic structure and the planes (110) and (110) in the monoclinic structure issubstantially lower and attractive vanderWaals forces are believed to dominate thecohesion forces between cellulose chains. Within these planes, thenumber of weak inter-chain hydrogen bonds in the Iβ structure is believed to be largerthan in the Iα polymorph and it has been suggested that it would contribute to thehigher stability of the Iβ form, as compared to the Iα form. The Iα hydrogen bonds thermally degrade at lower temperatures,contributing to the lower Iα thermal stability.[Moon et al, 2011]

In this way, this study focuses on the characterization of structure and thermalproperties of cellulose I, sometimes referred to as native cellulose. This workinvestigates the relationship between chemical l structure, hydrogen bond interactions,crystallite size and crystallinity and the influence of these parameters on the thermalstability and decomposition kinetics of cellulose fibers obtained by two differentpulping processes.



Fig(1.5): Hydrogen bond system of cellulose I

1.1.7.3 Crystal Structure

The order of the macromolecules in a cellulose fiber is not uniform throughoutthe whole structure. There exist regions of low order (so-called amorphous regions) aswell as of very high crystalline order. The experimental evidence available today isadequately interpreted by a two-phase model, the fringed fibril model, assuming loworder(amorphous) and high-order (crystalline) regions and neglecting the rather smallamount of matter with an intermediate state of order .The relative amount of polymerwithin the highly ordered regions is usually assessed from wide-angle X-rayscattering (WAXS) patterns or from the evaluation of a 13C CP-MAS NMR spectrum.The degree of crystallinity of cellulose (usually in the range of 40% to 60%) covers awide range and depends on the origin and pretreatment of the sample.[Klemm et al, 2005]

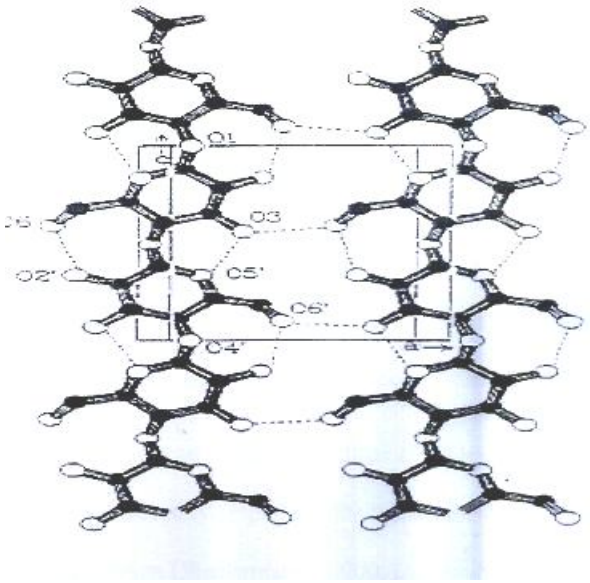


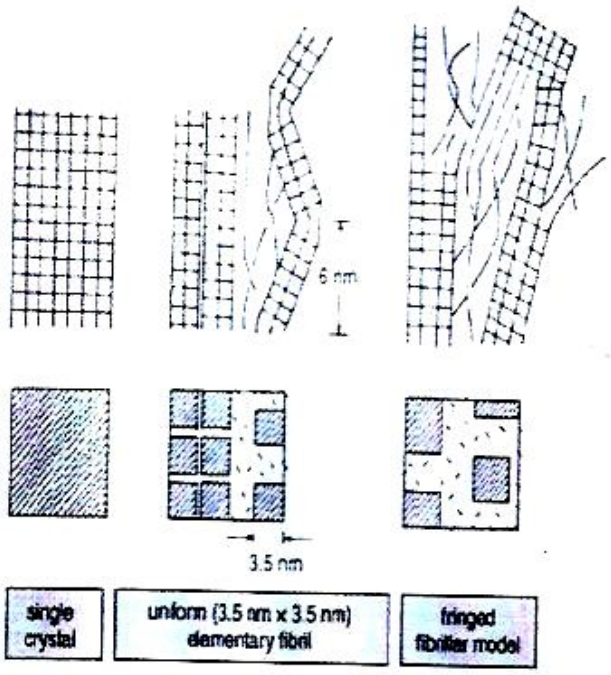
Figure (1.6): Most Probable Bond Pattern of Cellulose I

1.1.7.4 Morphology

The biological function and numerous applications of cellulose are based onits distinct fiber morphology. The morphological hierarchy is defined by elementaryfibrils, micro fibrils, and micro fibrillarybands . The lateraldimensions of these structural units are between 1.5 and 3.5 nm (elementary fibrils),between 10 and 30 nm (micro fibrils), and on the order of 100 nm (micro fibrillarybands). The length of the micro fibrils is on the order of several hundred nm.

The fringed fibrillary model with crystalline regions of varying dimensions(crystallites) and monocrystalline regions have been proven successful for thedescription of the structure of micro fibrils and the partial crystalline structure ofcellulose in connection with the reactivity of this polymer . The degree of crystallinity of cellulose and the dimensions of the crystalliteshave been the subject of extensive investigations for many years . Some results of X-ray diffraction measurements of native celluloses have beencompiled in notably, the lateral crystallite dimensions of regenerated cellulose(cellulose II) are in the range of 4–5 nm regardless of the production process where asin native celluloses, values of up to 20 nm have been observed. The reasons for theformation of nearly uniform cross-sectional dimensions of these cellulose IIcrystallites from different structure-forming processes still have to be clarified.

The pore structure can be considered the counterpart to the fibril morphologyof cellulose. It is considerably important for the accessibility in chemical reactionsand enzymatic degradation. The controlled variation of pore structures enables cellulose products tomeet the needs of a wide range of applications, from highly specialized membraneand carrier materials to consumer goods, such as nonwovens, withexcellent absorption properties.



Fig(1.7): Various models of the supramolecular structure of cellulose micro fibrils.

1.2 Extraction of cellulose from its natural source

1.2.1 Isolation

Isolation based on acidified sodium chloride is frequently applied to delignify wood materials as an initial step in the isolation of cellulose. [Loader et al., 1997] Alkali extraction to dissolve hemicelluloses before or after delignification is the common method. Treatment of the lignocelluloses materials with chlorite can remove almost all lignin at room temperature.[buchala and Fraser, 1972]

There are three methods of isolation

Delignification and alkali extraction method: This method is considered as the most efficient method for separating cellulose from straws and by releasing large amounts of lignin and hemicellulosic polysaccharides, respectively in particular, most of the lignins can be removed in a delignification step using chloride. Delignification can significantly facilitate the extraction of the hemicelluloses during alkali treatment and therefore result in the residues of cellulosic polymers having.[Josefsson et al., 5001]

Steam explosion method: In this method the signification amounts of hemicelluloses are partially hydrolyzed and lignins are depolymerized resulting in sugars and phenolic compounds that are soluble in water. Therefore, this process generally followed by fraction step such as alkaline extraction to separate the main cellulose components. [Sun et al., 2003]

Alkaline peroxide extraction method: This method exhibits good performance in isolation of cellulose. It is recently used to isolate complex from straws.[Graenacher, 1934]

1.2.2 Etherification of cellulose:

In the etherification of cellulose, N-alkylpyridinium halides is used, especially N-ethylpyridinium chloride and N-benzylpyridinium chloride. These solvents are used because of their high melting points, and were therefore diluted with organic solvents, such as dimethylsulfoxide (DMSO) and dimethylformamide (DMF) pyridine.[Zloang et al., 2004]

1.2.3 Acetylation

Acetylation of cellulose is carried out either in the presence or absence of base[Lewin, 2006]using acetic anhydride or acetic chloride as acetylating regent. Cellulos acetates are produced by reaction of cellulose with an excess of sulphuric acid or perchloric acid as the catalyst.[Myllmaki and Alcsela, 2005]

Acetylation of cellulose can also be found without a catalyst

1.3 Synthesis of Carboxymethylcellulose (CMC)s

Sodium carboxymethylcellulose (Na-CMC) was produced by conversion of alkali cellulose wollen in aqueous NaOH and a surplus of organic solvent (e.g. isopropanol, ethanol) with monochloro acetic acid (MCAA) or its sodium salt. The hydroxyl groups in cellulose are usually replaced by the carboxymethyl groups in the order of C2>C6> C3. [Heinze et al., 2005]

In practice, the manufacturing of CMC involves two steps (Scheme 1.5). In the first step, the cellulose is treated with NaOH, often in the presence of inert solvent, which act as both swilling agent and a dilatant and thus facilitate good penetration of NaOH into the cellulose structure. The alkali cellulose is accessible and reactive toward MCA, which is added to reaction in the second step. The reaction between alkali cellulose and the etherification agent carried out in aqueous system. According to the following reaction:

$$CeII - OH + NaOH + ClCH_2COONa \rightarrow Ce\ II - O - CH_2COONa +$$

$$NaCl + H_2O$$

A considerable amount of the etherifying agent, up to 30%, is consumed in side reaction with the aqueous NaOH forming predominantly sodium glycolate by hydrolysis of chloroacetate The CMC can be neutralized and dried immediately to give a technical grade or neutralized and washes to give a purified grade.

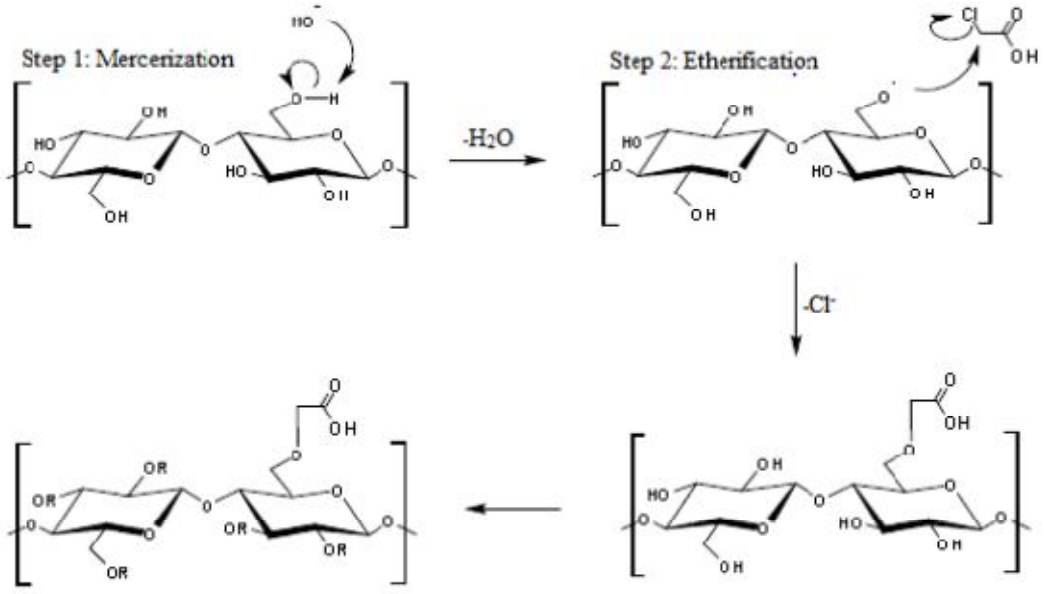


Fig (1.8):Carboxymethylation reaction

1.4 Applications of purified CMC

Cellulose derivatives being of natural origin have diverse physicochemical properties because of substituents DS, Molecular weight and degree of polymerization (DP) are reversed for their large scale use mainly as additives of fine / special chemicals in textile, pharmaceuticals, cosmetics, Food and backing industries.

CMC is non-toxic and it is currently finding an increasing number of applications in pharmaceutical, medical and food industries. It is a key component in control drug –release pills and in the manufacture of personal care products. It is also used in gels applied as protecting agent during heart throat and cornea surgery, most of the CMC application based on it is rheological properties. The ability of CMC to function as s thickener or flow-controlled agent depends largely on it is degree of substitution, molecular weight and stiffness of the cellulose back bone.

Applications of CMC span wide range of products and industries. CMC is used as thickening agent and purified CMC is used as a stabilizer in foods, particularly in dairy products such as ice cream, yogurt, and milk drinks, other food applications include beverages, syrups, baked goods, and pet foods. Other major industrial consumers that use purified CMC for its properties as a binder and thickener include producers of paper, the ceramics industry, and the textiles industry. Crude/unrefined CMC is used in laundry detergents as soil antired position aid, tobacco, cosmetics, foods, pharmaceuticals, adhesives, Aerial-drop fluids, Coatings and lithography.

Some applications for purified CMC illustrated in the following tables .

Table (1.1): Applications of CMC in Cosmetics industries

Specific application	Properties utilized
Toothpaste	Thickener; flavor stabilizer; suspending aid; binder
Shampoos; foamed	Suspending aid; thickener; foam stabilizer; high water- binding capacity
Creams; lotions	Emulsion stabilizer; film former; thickener
Gelled products	Thickener; gelling agent; film-former
Denture adhesives	Wet tack; long-lasting adhesion

Table (1.2): Application of CMC in Pharmaceuticals industries

Specific application	Properties utilized
Ointments; creams; lotions	Stabilizer; thickener; film-former
Jellies; salves	Thickener; gelling agent; protective colloid; film-former
Tablet binder; granulation aid	High-strength binder
Bulk laxatives	Physiologically inert; high water-binding capacity
Syrups	Thickener
Suspensions	Thickener; suspending aid

Table (1.3): Applications of CMC in Aerial drop fluids and Coatings industries

Specific application	Properties utilized
Insecticides	Thickener; binder; suspending aid
Drift-control agent	Thickener
Latex paints; paper coatings	Rheology control; suspending aid; protective colloid
Foundry core wash	Binder; thickener; suspending aid

Table (1.4): Applications of CMC in Foods Industries

Specific Application	Properties Utilized
Frozen desserts; soft-serve	Controls ice crystal growth; improves mouthfeel; body; and texture
Pet food	Water binder; gravy thickener; extrusion aid; binder of fines
Protein foods	Retains water; improves mouthfeel
Baked goods	Batter viscosifier; improves moisture retention and texture
Beverages	Suspending aid; rapid viscosifier; improves mouthfeel and body; protein stabilizer in acidified drinks
Desserts; icings; toppings	Odorless and tasteless; thickens; controls sugar crystal size; improves texture; inhibits syneresis
Low-calorie foods	No caloric value (2); thickens; imparts body and mouthfeel
Syrups	Clear; thickens; imparts favorable mouthfeel and body
Dressings; sauces	Thickener and suspending aid; imparts mouthfeel
Animal feed; extrusion Products	Lubricant; binder; film-former

Table (1.5): Applications of CMC in Detergents and Lithography and Tobacco Industries

Specific application	Properties utilized
Laundry	Whiteness retention through soil suspension
Fountain and gumming solutions	Hydrophilic protective film
Water-based inks	Binder; rheology control; suspending aid
Cigar and cigarette adhesive	Good wet tack; high film strength
Reconstituted sheet	High -strength binder and suspending aid

1.5 previous study

Many studies were handled for converting cellulose extracted from different natural resources to carboxymethylcellulose (CMC). Many parameters were considered to optimize the yields, Degree of substitution (DS) value and rheological behavior of the synthesized CMC material.

Pushpamalar*et al*., (2006) isolated cellulose from sago waste and converted it to CMC by etherification using sodium monochloroacetate in the presence of sodium hydroxide. The reaction was optimized against temperature, concentration of NaOH and reaction time. The optimized product has a large value of DS of 0.821. The optimized DS value was obtained using pure isopropyl alcohol as the solvent medium, reaction period of 180 min, 6.0 g of sodium monochloroacetate, 10 mL of 25% NaOH aqueous solution and a reaction temperature of 45 °C. Fourier Transform Infrared (FT-IR) spectra were used to characterize the CMC product.

Adinugraha and Marseno, (2005) studied the synthesis and characterization of Na-CMC from Cavendish banana pseudo stem. The cellulose powder was extracted using an aqueous solution of 8% NaOH at 100 °C for 3.5 h, and then bleached with an aqueous solution of 5% NaOCl at 30 °C for 3 h. The cellulose was then alkalized with 5–30% NaOH at 25 ºC for 1 h then variable quantities of 3-7 g of $ClCH_2COONa$ were added per 5 g cellulose. The results showed that the cellulose alkalized by 15% NaOH gave CMC of the optimum properties, i.e. DS of 0.75, viscosity of 4033 cps, purity of 98.63 % and crystallinity of 38.33 %.

Aguir and M'henni, (2006) studied the production of CMC from bleached cellulose pulps obtained from *Posidoniaoceanica*. The carboxymethylation reaction was carried out with NaOH and monochloro acetic acid (MCA) as the reagent. The highest DS (2.75) was obtained with *n*-butanol at an optimum temperature of 80 °C. The best molar ratios of cellulose/NaOH and cellulose/MCA were 1/3.

Hutomo*et al.*, (2012) studied the synthesis and characterization of Na-CMC from pod husk of Cacao. The optimum conditions used to produce CMC of higher DS value of 0.75 were 15% NaOH, temperature 55.93°C, 4g NaMCA and 3h reaction period. The aqueous solution of CMC of the highest DS value (0.75) exhibited viscosity of 206.10 cps.

Varshney*et al.*, (2006) synthesized CMC from cellulose isolated from Lantana camara, using optimized set of conditions include 20% NaOH aqueous solution, an amount of MCA of 2.05 mol/AGU, carboxymethylation time of 3.5 h, temperature of 55 °C and isopropyl alcohol as a solvent medium. The resulting CMC had a viscosity of 600 cps (1% solution) and 7500 cps (2%solution) and DS value of 1.22.

Haleem*et al*., 2014 studied the synthesis of CMC from waste of cotton ginning (CGW) industry. The isolated cellulose was converted to CMC by etherification reaction using Na-MCA and different concentrations of sodium hydroxide (NaOH) (5 – 40 g/100 mL). The optimum NaOH concentration for the carboxymethylation reaction was found to be 20 g/100 mL NaOH which provided the highest DS value (0.874). The aqueous solution of optimized CMC exhibited the highest viscosity.

Mat Som, (2004) studied the preparation and characterization of CMC from oil palm empty fruit bunch fibers. The work involved manipulation of three variable parameters namely, reaction temperature (55, 60 and 70 °C), time of reaction (4, 6, 8, 16, 18 and 20 h) and concentration of sodium hydroxide (2.6 moles and 3.4 moles per mole of monochloro acetic acid). Thirty-six grades of CMC material were produced and characterized. The findings showed that the percent yield of CMC, moisture content, DS, purity, viscosity and ash content were in the range of 49.76 – 58.62%, 7.3 – 8.8%, 0.74 – 0.95, 85.5 – 99.5%, 116 – 2217 cps and 15.2 – 20.2%, respectively.

Overall judgment on the selection of the best processing conditions was preferably of 55 °C, 2.6 moles NaOH and 4 h reaction time. The conversion of cellulose to CMC material was indicated from the FT-IR spectra of as-synthesized and commercial CMC materials. Both materials exhibited similar patterns with the presence of peaks at the fingerprint regions between 1300 and 1580 cm-1 due to the presence of carboxymethyl group.

Latif*et al*., (2007) studied the synthesis and characterization of CMC from rayon grade wood pulp and cotton linter. The dried cellulose was alkalized using 40% NaOH solution at 25 °C for 1.5 hour. The carboxymethylation reactions were conducted using various amounts of

Na-MCA (5-7g) per 5 g of cellulose, a temperature of 55 °C, reaction time of 3.5 h and isopropyl alcohol solvent. The optimum DS value of the synthesized CMC was found to be 1.9.

Heydarzadeh*et al.*, **(**2009) studied the catalyst-free conversion of alkalized cellulose to fine CMC at mild conditions**.** The preparation of CMC was conducted using sodium hydroxide solution in sequential reactions involve MCA species at desired conditions. CMC has been successfully synthesized in a batch reactor with DS value of 0.15 to 0.7 and excellent purity of 99.3% at pH 7. The maximum DS of 0.7 was obtained using 40% monochloroacetate (MCA) and 30% NaOH. The samples of CMC were characterized by SEM and FT-IR spectroscopic techniques. The synthesized CMC was easily dissolved in water and was found to be of pharmaceutical and food grade.

Joshi *et al.*, (2015) studied the synthesis and characterization of CMC from mixed office waste papers (MOW). After deinking, the cellulosic pulps of MOW papers were functionalized with carboxymethyl group to give CMC of high value of DS. The carboxymethylation process was completed using NaOH and $ClCH_2COONa$ in an alcoholic medium. Maximum DS value of 1.07 was obtained by conducting the reaction process at 50 °C for 3 hours using solutions of 0.094 M NaOH and 0.108 M $ClCH_2COONa$.

1.6 Objectives

The objectives of this study were to:

- Investigate and characterize the stabilizer.
- Determine sodium chloride percent.
- Determine free glycolate percent.
- Determine CMC percent in the stabilizer.

Chapter Two

Materials and Methods

Chapter two

Materials and Methods

2.1Materials

Stabilizer sample, copper sulfate, distilled water napthol TS and sulfuric acid.

2.1.1 Methods

2.1.1.1 Foam test

A 0.1% solution of the sample was vigorously shaked. No layer of foam appeared.

2.1.1.2 Precipitate formation

5 ml of a 5% solution of copper sulfate was added to 5 ml of a 0.5 % solution of the sample . A precipitate appeared.

2.1.1.3 Color reaction

0.5 g of powdered carboxymethylcellulose sodium were added to 50 ml of water, while stirring to produce a uniform dispersion. Stirred until a clear solution was produced. 1 ml of the solution, diluted with 1 ml of water, put in a small test tube, 5 drops of 1-naphthol TS were added to the diluted solution. The test tube was inclined, and 2 ml of sulfuric acid were carefully introduced down the side of the tube so that it forms a lower layer. A red-purple colour develops at the interface.

2.2. Purity

2.2.1 Materials

Stabilizer sample, nitric acid, silver nitrate, ammonium thiocyanate glacial acetic acid, distilled water, acetone, sulfuric acid and ammonium carbonate.

2.2.2.1 Sodium chloride

5 g of the sample was heated, in porcelain crucible, first with a small flame so that the sample does not ignite and then, when the charring is complete, then heated further in an electric oven for 15 min at about 500C^{o}. After cooling, the ashes were pulverized thus obtained and extracted several times with warm water. The extracts were but into a 500-ml volumetric flask, acidified with nitric acid and diluted to the mark. The NaCl content of 100 ml of this extract was determined by the method of Volhard, using 0.02 N silver nitrate and 0.02 N ammonium thiocyanate. Each ml of 0.02 N silver nitrate is equivalent to 1.169 mg of NaCl. The sodium chloride content was calculated by the formula:

$$\%NaCl = \frac{a \times 0.001169 \times 5}{b} \times 100$$

Wherea is ml of 0.02 N silver nitrate used

b is dry weight of 5 g of the sample

2.2.2.2 Free glycolate

0.5 g of the sample were weighed, and transferred to a 100-ml beaker. The sample was moistened thoroughly with 5 ml of glacial acetic acid, followed by 5 ml of water, and stirred with a glass rod for about 15 minutes until the solution is complete. Then 50 ml of acetone were slowly added while stirring and then approximately 1 g of sodium sulfate. Then stirred for several minute till a complete precipitation of the carboxymethyl cellulose was noted. Then filtered through a soft, open-texture paper, previously wetted with a small amount of acetone, the filtrate was then collected in a 100-ml volumetric flask. 30 ml of acetone was used to facilitate the transfer of the solids and to wash the filter cake. A volume with acetone and mix was made up.

A blank solution containing 5 ml of water, 5 ml of glacial acetic acid and acetone was prepared in another 100-ml volumetric flask. 2 ml of the sample solution and 2 ml of the blank solution were pipet into two 25-ml volumetric flasks. The acetone was removed by heating the uncovered flasks upright in a boiling water bath for exactly 20 min. Cooled to room temperature then 5 ml of 1-naphthol were added, mixed thoroughly, then 15 ml more of the TS were added and mixed. The mouth of the flask was then Covered with a small piece of aluminum foil and heated upright in the boiling water bath for 20 min. Cooled to room temperature and made up to volume with 1- naphthol.

The absorbance of sample solution was measured against blank solution at 540 nm using 1-cm cells. The corresponding mg of glycolic acid from the calibration curve obtained as follows:

0, 1, 2, 3 and 4-ml aliquots of standard glycolic acid solution (1mg per ml, prepared by weighing accurately 0.100 g of glycolic acid, previously dried in a vacuum pipet for at least 16 h, and then dissolving in 100 ml of water; do not keep the solution longer than 30 days) were introduced into a series of five 100-ml volumetric flasks. Water was added to each flask to a volume of 5 ml, then 5 ml of glacial acetic acid was added and made up with acetone to mark and mix. 2 ml of each solution (containing, respectively, 0, 1, 2, 3, and 4 mg of glycolic acid per 100 ml) were pipet into a series of five 25-ml volumetric flasks and proceeded in the same manner as described for the Test Solution. The mg of glycolic acid in the original 100 ml of solution plotted against absorbance gave a calibration curve. The sodium glycolate (free glycolate) content was calculated by the formula:

$$\%\, sodiumglycolate = \frac{a \times 0.0129}{b}$$

Wherea is mg of glycolic acid read from the calibration curve

b is g of dry-weight of the sample

2.2.2.3 Degree of substitution

Sample preparation

5 g of the sample were weighed and transferred into a 500-ml conical flask. 350 ml of methanol (80% by volume) were added. The suspension was shaken mechanically for 30 min. Decanted through a tared glass filtering crucible under gentle suction.The treatment was repeated with the extraction liquid until the test for chloride ions with a solution of silver nitrate TS was negative. The sodium carboxymethyl cellulose was Transferred into the same crucible. The extraction liquid that adheres to the substance with acetone was displaced. The crucible was dried in an oven at 110^{o} cooled and weighed repeatedly until constant in weight.

Procedure

2g were weighed, of the bone dry substance, obtained with the above-mentioned alcohol-extraction procedure, in a tared porcelain crucible. Initially, charred carefully with a small flame and afterwards for 10 min, with a large flame. The residue was the Cooled and then moistened with 3-5 ml of concentrate sulfuric acid. Heated cautiously until the fuming is finished. After some cooling about 1 g of ammonium carbonate was added, by distributing the powder over the whole contents of the crucible.Heated again, initially with a small flame until the fuming is finished and heated then at a dull red heat for 10 min. The crucible was placed for 1 h in an oven at about $600C^{o}$.

The sodium content of the alcohol-extracted sample was calculated by the formula:

$$\%\ sodium = \frac{a \times 32.38}{b}$$

Wherea is the weight of residual sodium sulfate

b is the weight of the alcohol-extracted dry sample

Calculate the degree of substitution by the formula:

$$Degree\ of\ substitution = \frac{162 \times \%sodium}{2300 - (80\% \times \%\text{sodium}}$$

Method of assay

The percentage of sodium carboxymethyl cellulose in the sample was calculated by subtracting from 100% the sum of the percentages of sodium chloride and sodium glycolate (free glycolate), determined separately by the procedures above.

Content% = 100 - (% NaCl + % sodium glycolate)

Chapter three

Results and discussion

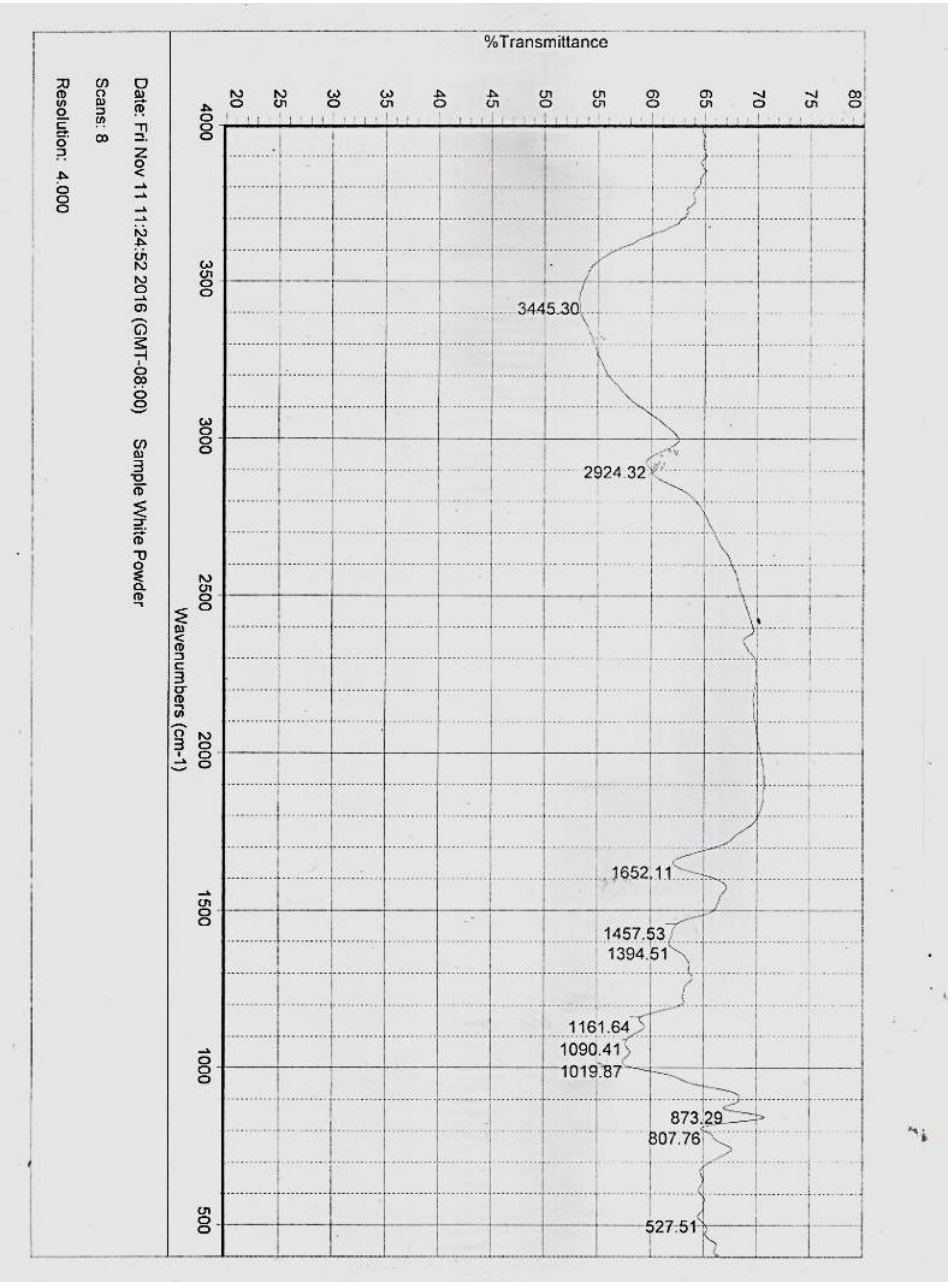
Chapter three

Results and Discussion

3.1 Characteristics of CMC by Infrared (IR)

FT-IR spectroscopy was used to indicate the presence of carboxymethyl group, it was also used to examine other group in the product.

The notable peak at 3445 cm^{-1} O-Hst vib as intramolecular and intermolecular hydrogen bond, 2924 cm^{-1} is C-H st vib, peak from 1457 cm^{-1} to 1652 cm^{-1} indicate of presence of carboxymethyl celluose, peak, at 1393 cm^{-1} is OH bending peak at 1090 cm^{-1}OCH-O-CH_2 st.



Infrared spectrum CMC with DS of 0.2 was shown above, The peaks at wave number of 1652 and 1457 indicated of presence of carboxymethy cellulose. According to Djagaw.Marseno (2005), carboxyl group, peaks appear at wave number of 1652 cm^{-1} And 1394-1457 cm^{-1} the peaks at wave numbers of 2924 cm^{-1} and 3445 cm^{-1} here attributed to contamination from impurities or combination band from water.

3.2 Sodium Chloride Percent

$$\%NaCl = \frac{a \times 0.001169 \times 5}{b} \times 100$$

Where

a = 4.15 cm^3

b = 5 g

Therefore

$$\% \text{ NaCl} = \frac{4.15 \times 0.001169 \times 5}{5} \times 100$$

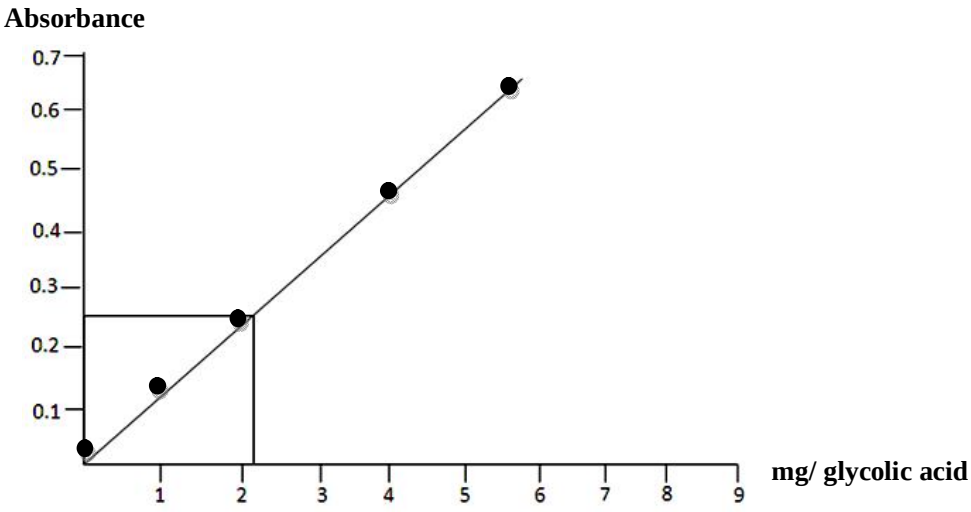
$$= 0.4851\%$$

3.3 Free GlycolatePercent

Absorbance of the sample = 0.268

Mg of glycolic acid	absorbance
0	0.000
1	0.110
2	0.260
3	0.467
4	0.668

mg of Glycolic acid Vs absorbance



Soduim glycolate (free glycolate) aontent calculated by the formula:

% Sodum glycolate = $\frac{a \times 0.129}{b}$

Where:

a is mg of glycolic acid read from the calibration curve (0.268 g)

b is g of dry – weight of the sample (0.5g)

there fore:

% sodium glycolate = $\frac{2.3 \times 0.129}{0.5} \times 100\% = 0.5934\%$

3.4 Degree of Substitution

Firstly the sodium content of the of the alcohol extracted sample by the formula

$$\%\text{sodium} = \frac{a \times 32.38}{B} \times 100$$

Where

a= 0.2118

b= 2.7831

Therefore

$$\%\text{sodium} = \frac{0.2118 \times 32.38}{\mathbf{2.7831}} = 2.4642\%$$

Degree of substitution

$$= \frac{162 \times \%\ \text{sodium}}{\mathbf{2300 - (80 \times}\ \%\ \text{sodium)}}$$

$$\frac{162 \times 2.4642}{\mathbf{2300 - (80 \times 2.4642)}} = 0.1898$$

3.5 Assay: (Percent of CMC)

Content % = 100 – (Nacl+%sodium glycolate)

There fore

= 100 – (0.4851 + 0.5934)

= 98.9215%.

3.6 Conclusion

The present of Sodium Carboxymethy cellulose was characterize Successfully it was found to be 98.92%, sodium chloride and sodium free glycolate were determined it was found to be 0.48, 0.59% respectively. Ds value were determined it was found to be 0.2.

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