# CHAPTER 4

# SYNTHESIS AND CHARACTERIZATION OF *N*-SUBSTITUTED CHITOSAN DERIVATIVES AND THEIR APPLICATION ON COTTON FABRIC

## 4.1 INTRODUCTION

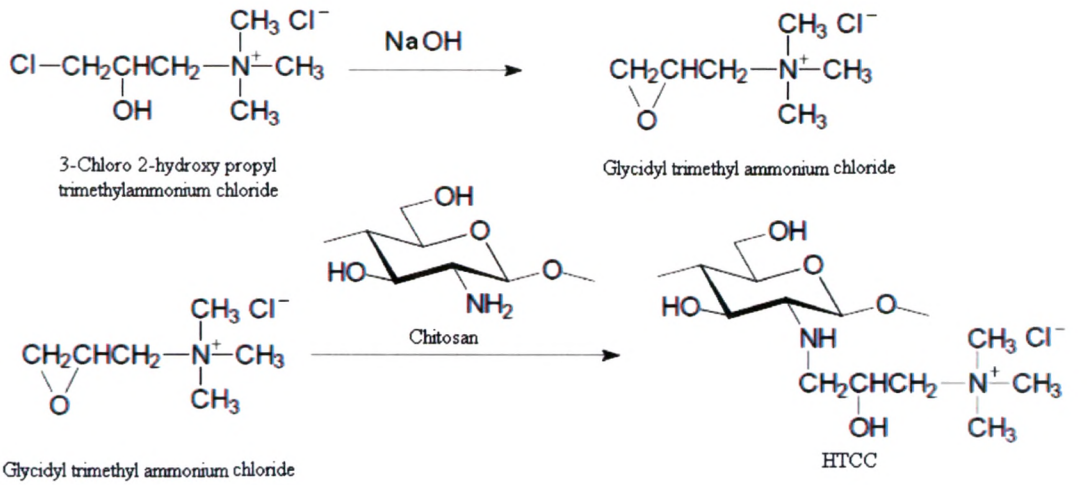
The application potential of chitosan biopolymer on cotton textiles is revealed in previous chapters. By virtue of polycationic nature and film forming properties, chitosan has proved a useful auxiliary in dyeing and finishing of cotton fabric. A substantial improvement in dyeability of chitosan treated fabric towards direct dyes from salt free dye bath was noticed. Post dyeing treatment of chitosan showed intensified colour value and improved fastness to washing. Resistance to microbial attack was also found to be improved. Besides improvements in these properties, the chitosan treated fabric, however, encountered several challenges. One of the major drawbacks of chitosan was its limited solubility in neutral or alkaline aqueous medium. Highly acidic pH required for solubility of chitosan resulted into hydrolytic degradation of fibre due to curing at elevated temperature.

The chitosan, due to higher viscosity and hence the rigid film deposited on surface of fibre, imparted undesired stiffness and harshness with result of loss in inherent appeal of cotton fibre. Further the appearance and wrinkle recovery property were found to be deteriorated. Lowering of viscosity by depolymerization of high molecular weight chitosan could not meet the requirements; on the other hand an excessive yellowness was imparted.

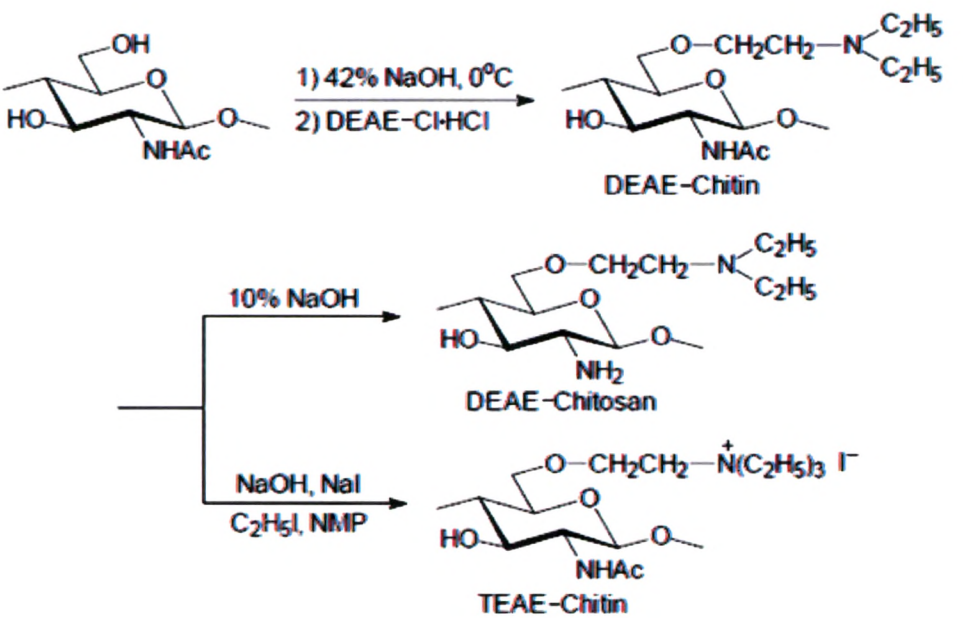
An emerging technology i.e. nano technology was adopted wherein the particle size of chitosan was scaled down to near nano level by ionic gelation with pentasodium tripolyphosphate (TPP). This enabled a greater penetration of polymer into the fibre structure and increased its effectiveness even at very low concentrations. Various properties, mentioned above, were found to be significantly improved. Nevertheless, stability of nano CHT dispersions was extremely limited and therefore standing bath stability was restricted to 24h.

In all cases, one of the severe problems encountered was loss in strength and whiteness due to chlorine retention (discussed in detail in section 4.3.2.3). Chlorine retention mainly arises due to the presence of free -NH- groups [1] which form chloramines with chlorine in presence moisture particularly in absence of alkali causing the yellowness. Chloronitrogen compounds thus formed liberate hydrochloric acid during heat treatments like pressing under moist condition, which damage the cloth. A very similar kind of problems often found in finishing treatments with aminoplasts and cationic softeners containing free -NH- groups [2, 3] as illustrated in scheme 4.13. In order to avoid or minimize such damages due to either acid hydrolysis during curing process or due to chlorine retention, structural modifications in chitosan are essential such that aqueous solubility at almost neutral pH is obtained and /or modifying the amino functional groups by replacing their free protons by other stable groups so that no sites available for chlorine retention. The limited solubility of chitosan in aqueous media can be overcome by introducing new functionalities through its derivatization such as, for instance, such as sulphonation [4], sulphation [5], carboxymethylation [6], grafting [7, 8] etc reactions. Grafts of chitosan and polyacrylic acid have shown very high water-sorbing ability (~ 600% w/w) [9]. Such reactions, however, also add an anionic nature to the cationic polyelectrolyte character of the parent chitosan [10]. These reactions, often, occur at hydroxyl reactive sites [11]. *N*-substituents containing water dissolving moieties can be obtained by selectively by halogen displacement reaction [12] or by reductive amination [13] to produce products like *N*-caboxymethyl chitosan, *N*-carboxypropyl chitosan etc derivatives.

An alternative route to improve the water solubility of chitosan without changing its cationic character is the introduction of an enough number of permanent positive charges in its chains. One such method is the attachment of substituent bearing quaternary ammonium terminal group. A product containing *N*- substituted quaternary ammonium salt namely *N*-(2-hydroxy) propyl -3-trimethyl ammonium chitosan chloride (HTCC) was synthesized by Daly and Guerrini [14] by using a compound that produces the glycidyl reagent *in situ* such as 3-chloro-2-hydroxy propyl trimethylammonium chloride, a commercially available stable compound Quat 188, developed (Scheme 4.1) This Chitosan derivative (HTCC) shows excellent solubility in neutral water.




**Scheme 4.1** Synthesis of *N*-(2-hydroxy) propyl -3-trimethyl ammonium chitosan chloride (HTCC)




**Scheme 4.2** Synthesis of *O*-substituted quaternary ammonium chitin and chitosan

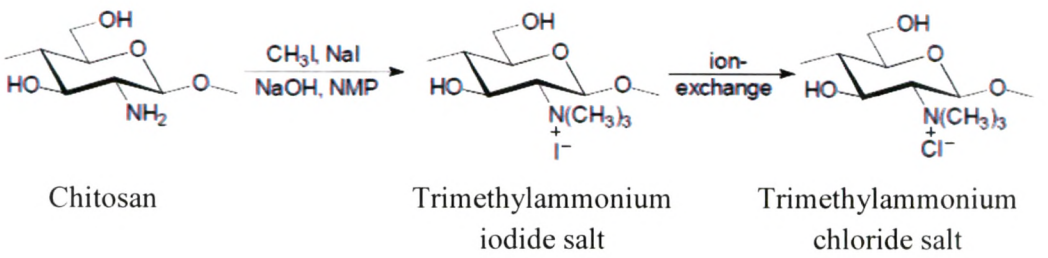
Quaternary ammonium group containing substituents can also be attached through *O*-substitution reaction. Kim et al [15] obtained triethylaminoethyl derivative of chitin

(TEAE-Chitin). It was synthesized by first activating the C-6 primary hydroxy group in chitin at low temperature. The activated chitin was then allowed to react with diethylaminoethyl chloride (DEAE) to produce DEAE-Chitin derivative, followed by quaternization using ethyl iodide. Interestingly, the intermediate DEAE-Chitin derivative was also found soluble at neutral pH. These products on deacetylation gave chitosan derivatives as illustrated in scheme 4.2

All these reactions, however, could not obviate the free -NH- groups completely and the problems associated with chlorine retention still persisted. Modifications of amino groups of chitosan or above derivatives though substitution reactions such as complete alkylation or in other words direct quaternization of amino groups can produce chitosan tri alkyl ammonium halide salts or quaternary ammonium salts which are totally -NH- free. A simplest derivative in this class is the trimethylammonium salt of chitosan. It is obtained by repeated treatment of chitosan in *N*-methyl-2-pyrrolidone (NMP) containing sodium iodide and methyl iodide in presence of sodium hydroxide. An anionic exchange of iodide with chloride ion may be necessary due to stability issues. The quaternization reaction is shown in scheme 4.3. Bayat et al [16] studied the effect of sodium hydroxide and methyl iodide concentration on degree of quaternization and found these to be the most effective reaction variables. Most of previous researchers have followed the same protocol for the synthesis of chitosan alkyl ammonium halide salts [17-20]. Attempts have also made in synthesizing *N*-methyl chitosan derivatives in acidic medium, as reviewed by Achwal [21] from German literature. In this method, chitosan was dissolved in 1% acetone and pH was adjusted to 6.3 and then refluxed at boil with excess methyl iodide for 10h.

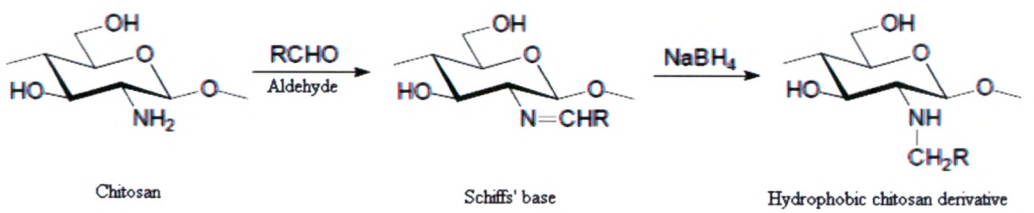
Reductive amination i.e. Bosch reduction of Schiff's base provides an attractive route for the synthesis of *N*-substituted chitosan compounds containing alkyl or aryl groups of varying chain lengths or molecular sizes. Primary amines when treated with alkyl or aryl aldehydes produce Schiff's base which on reduction with $NaBH_4$ or $NaBH_3CN$ results into *N*-alkyl or aryl substituent becoming secondary amine [22] as shown in scheme 4.4. Since the reaction is carried out in acidic medium, a great degree of homogeneity is favored. These secondary amines then can further be quaternized with alkyl iodide similar to scheme 4.3. A series of chitosan quaternary ammonium salts

containing *N*-alkyl and/or *N*-aryl substituents were prepared by different workers for various purposes are reported [16, 18, 23-28].




Chitosan | Trimethylammonium iodide salt | Trimethylammonium chloride salt

**Scheme 4.3** Synthesis of trimethylammonium salt of chitosan




Chitosan | Schiffs' base | Hydrophobic chitosan derivative

**Scheme 4.4** Synthesis of hydrophobic chitosan derivatives: Bosch reduction

Studies related to synthesis, properties and applications of chitosan derivatives such as quaternary ammonium salts, *N*-alkylated, *N*-arylated and combination of these are reported in literature. Muzzarelli and Tanfani [29] followed the reductive amination Schiff's base and then methylation of N-alkyl chitosan to generate prepared *N*-trimethyl chitosan iodide salt. This three step method was found to reduce DP of main chain and resulted side reactions such as *O*-substitution. This effort was made, aiming its application as antibiotic and ion exchange material. Britto and Assis used dimethylsulfate for obtaining quaternary ammonium salt [30].

With respect to its physical and chemical properties several works have been published. Curti and Filho [31] studied the viscosity behaviour of trimethyl chitosan chloride salt. Their study showed that the chitosan and trimethyl chitosan chloride exhibit a linear decrease in intrinsic viscosity as a function of reciprocal square root of the ionic

strength. The molecular weight was found to be affected due to quaternization maintaining the chain stiffness intact. Snyman et al [19] prepared varying degree of trimethyl chitosan chloride by repeated quaternization treatments. The weight average molecular weight and intrinsic viscosities were found to be decreased with increase in degree of quaternization due to repeated processes. Britto et al. [32] observed the changes in mechanical properties due to *N*-methylation of chitosan. Films of chitosan and trimethyl chitosan presented viscoelastic behaviour, where in the former exhibited elastic behaviour with greater elongation while the latter had small modulus of elasticity and typical viscous behaviour. These authors [33] also reported a kinetic study on thermal degradation of trimethyl chitosan.

Murata et al. [34, 35] reported the cytotoxic activity and the formation of polyelectrolyte complex trimethyl chitosan with DNA. Kean et al. [36] and Thanou et al. [37] published results of a study about the toxicity and transfection efficiency of trimethyl chitosan derivatives with respect to the degree of quaternization. As trimethyl chitosan gained attention for use in oral drug delivery, some reviews on the subject have appeared [38 - 40]. The quaternary ammonium salt using glycidyl trimethylammonium chloride as the quaternizing agent was found to be useful in cosmetic applications [14]. Kotze et al. [41] found a superior efficiency as absorption enhancer for hydrophilic drugs across intestinal epithelia than the chitosan itself.

Various long chain alkyl substituents have resulted in chitosan derivatives with varying degree of hydrophobicity. Such materials are industrially important as they show unusual and interesting rheological properties thought to arise from the intermolecular association of neighboring hydrophobic substituents [42]. More recently, an important branch of application for chitosan quaternary salt related to antimicrobial action has gained attention. It started by Kim et al. [23, 43] testing several chitosan quaternary salt against *Staphylococcus aureus*. In this way, the authors described the reaction of chitosan with formaldehyde, butyraldehyde, n- octyl aldehyde, and n-dodecyl aldehyde, treated the resulting Schiff's bases with sodium borohydride, obtaining the quaternary salts via methyl iodide synthetic route. In fact, the antibacterial activity of the prepared salts was higher than that found for chitosan itself and increased with increasing chain length of the alkyl substituent. Jia et al. [44], also prepared several quaternary chitosan salts and tested

against gram-negative bacteria *Escherichia coli*. It was seen that these salts exhibited higher *in vitro* activity against *E. coli* than chitosan, mainly in acid medium. Particularly, other combinations including alkyl, aryl moieties and carboxymethylation in chitosan quaternary salt also showed to be efficient against gram-negative and gram-positive bacteria [27, 45-47]. Effect of different *N*-substituents on insecticidal and fungicidal activity of chitosan is presented by Rabea et al [24, 25]. They found all the *N*-alkylated and *N*-benzyl chitosan derivatives higher fungicidal activity than parent chitosan against *Botrytis cinerea* and *Pyricularia grisea*, and a derivative *N*-(2-chloro 6-fluorobenzyl) benzyl chitosan as a most effective insecticide.

The utmost research is the synthesis and application of chitosan quaternary salts as nanoparticles. The most popular method of preparation of nano dispersion of chitosan quaternary salts is based on ionic gelation process with TPP. Xu et al. [48] synthesized *N*-(2-hydroxyl) propyl -3-trimethyl ammonium chloride nanoparticles. They described nanoparticles in the size range of 110 to 180nm with enhanced protein carrier efficiency. Several other important applications have emerged for chitosan trimethyl ammonium salts nanoparticles, such as nasal [49, 50] and oral vaccine delivery system [51]; and insulin releaser [52].

Thus, broadly speaking, the applications of these chitosan derivatives are emphasized mostly in medical domain such as gene delivery tool, controlled drug release system, as absorption enhancer for hydrophilic drugs transport across epithelium, antibiotics and, in cosmetics. However, very few applications of chitosan quaternary ammonium salts on textiles are reported. Most of the applications studied were antimicrobial concern. Kim et al.[53] treated the cotton fabric with HTCC and studied the effect on antimicrobial property. At very low concentration, such as 0.025% o.w.b., HTCC showed very superior antibacterial property, indicated by almost 100% reduction in bacteria as against only 30% reduction in bacteria in case of 1% chitosan. Lim and Hudson [54] treated the cotton fabric with fibre reactive chitosan derivative containing quaternary ammonium groups, *O*-acrylamidomethyl- *N*-(2-hydroxy) propyl -3-trimethyl ammonium chitosan chloride (NMA-HTCC) and evaluated its effect on dyeing with direct and reactive dyes; and antibacterial properties. They reported enhanced dye uptake with zero salt concentration with improved fastness properties. The antibacterial effect of

cotton treated with 1% NMA-HTCC, however, was almost lost after dyeing. This was attributed to the blocking of cationic groups. The undyed cotton fabric treated with 1% NMA-HTCC, on the other hand, showed 100 % reduction in bacteria which was sustainable for 50 wash cycles as against only 30% bacterial reduction by parent chitosan. Gleanings from German literature by Achwal [55] reported the after treatment with *N*-methyl chitosan derivative showed good improvement in fastness of direct dyeings comparable with conventional synthetic products.

The present research work, therefore, has been aimed at preparing a series of chitosan derivatives belonging to *N*-substituted quaternary ammonium salts having enhanced hydrophilicity and reducing free of -NH- groups presence to capture chlorine in any post treatment. Trimethyl chitosan chloride (TMCHT) was synthesized by the reaction of chitosan (CHT) with methyl iodide in alkaline medium followed by ion exchange with sodium chloride. In another series of chitosan derivatives, *N*- alkyl and *N*-aryl substituted chitosan of varying molecular size of substituents through the reductive amination of Schiff's base obtained by the reaction of chitosan with respective aldehydes were synthesized. The quaternization of *N*-substituted derivatives were then performed by the reaction of these compounds with methyl iodide as was carried out for TMCHT. The selected *N*-alkyl chitosan derivates were *N*-ethyl chitosan (N-Et CHT), *N*-butyl chitosan (N-Bu CHT) and *N*-dodecyl chitosan (N-Dod CHT) and that of *N*-aryl substituents were *N*-benzyl chitosan (N-Bz CHT) and *N*-(1-Naphthyl) methylene chitosan (N-Np CHT) derivatives. These *N*-synthesized chitosan derivatives were further quaternized with methyl iodide in alkaline medium. Various techniques employed for characterization of these derivatives were FTIR spectroscopy, $^{1}$HNR spectroscopy, Elemental (CHN) analysis and conductometry. Various reaction parameters such as methyl iodide concentrations, alkali concentration and the role of co-solvent (NMP) on degree of quaternization of chitosan were studied. The further study performed also include effect of chain length of alkyl substituent and molecular size of *N*-aryl substituent on degree of substitution on CHT and also on then quaternization (DQ) of *N*- substituted CHT derivatives.

Trimethyl chitosan chloride (TMCHT) of varying degree quaternization and *N*-substituted CHT of similar level of DS and the quaternized derivatives of maximum DQ

on these selected *N*- substituted CHT were applied to cotton fabrics by pad dry cure method. Effect of these *N*- substituted CHT derivatives at different concentrations on the appearance, feel, chlorine retention, absorbency, dyeing behaviour with direct dyes that including both pre and post dyeing treatment were studied. Absorbency was determined by drop penetration method and handle by measuring the bending length. The dyeing behaviour was also extended to evaluate the stoichiometry by dyeing with acid dye. Appearance and dyeing results were examined on computer colour matching systems in terms of whiteness, yellowness brightness indices and K/S values respectively. The effect of CHT derivatives on cotton fabric was also studied for various aesthetics and value additions such as wrinkle recovery, soil release and antimicrobial properties. The resiliency was determined by crease recovery angle and compared with commercial aminoplast resin. The soiling tendency towards oily soil was evaluated both gravimetrically and optically on CCMS. Resistance to microbial attack was studied by evaluating the strength loss due to rotting under composted soil bed i.e. soil burial test.

## 4.2 MATERIALS AND METHODS

### 4.2.1 Fabric

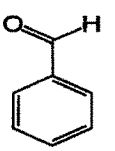
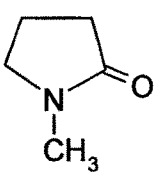
The same fabric as specified in chapter 2, section 2.2.1 was used.

### 4.2.2 Dyes and chemicals

The details of various chemicals employed in present research investigation are given in Table 4.1.

Dyes namely C.I.Direct Red 81, C.I.Direct Blue 71, C.I. Acid Blue 158 and chemicals namely Chitosan (CHT), DMDHEU etc used were the as specified in chapter 2, section 2.2.1. and other chemicals such as acetic acid ($CH_3COOH$), acetone ($CH_3COCH_3$), Glauber's salt ($Na_2SO_4$), methyl alcohol(CH3OH), magnesium chloride ($MgCl_2$), potassium iodide (KI), sodium iodide (NaI), sodium hydroxide (NaOH), sodium chloride (NaCl), soda ash($Na_2CO_3$), silver nitrate ($AgNO_3$) etc used were of analytical grade obtained Qualikem Fine Chemicals Pvt Ltd, Vadodara. Double distilled was employed for all synthesis and analytical purposes.

**Table 4.1** Specifications of various chemicals

| Sr no | Name and Supplier | Specifications |
|---|---|---|
| 1. | Methyl Iodide (MeI), Qualikems Fine Chem Pvt. Ltd | Grade: Analytical, Purity 99%, Mol.wt 142, Density 2.28g/cc<br>Molecular Formula: $CH_3I$ |
| 2. | Acetaldehyde (35%), s.d.fine chemicals Ltd, Mumbai | Grade A.R, Purity 35%, Mol wt 44.05, Density 0.78 g/cc<br>Chemical Formula: $CH_3CHO$ |
| 3. | n-Butyraldehyde Spectrochem Pvt Ltd, Mumbai | Grade: Analytical, Purity 99%, Mol wt 72.11, Density 0.8 g/cc<br>Chemical Formula: $CH_3(CH_2)_2CHO$ |
| 4. | Dodecyl Aldehyde Acros Organics Fisher Scientific | Grade: Analytical, Purity 92%, Mol wt 184.32, Density 0.83 g/cc<br>Chemical Formula: $CH_3(CH_2)_{10}CHO$ |
| 5. | Benzaldehyde Finar Chemicals Ltd., Ahmedabad | Grade: Analytical, Purity 99%, Mol wt 106.13, Density 1.044 g/cc<br>Chemical Formula: $C_6H_4CHO$<br>  |
| 6. | 1-Napthaldehyde Acros Organics Fisher Scientific | Grade: Analytical, Purity 95%, Mol wt 156.18, Density 1.15 g/cc<br>Chemical Formula: $C_{10}H_7CHO$ |
| 7. | Sodium borohydride Qualikem Fine Chemicals Pvt Ltd, Vadodara | Grade: Analytical, Purity 97%, Mol wt 37.83,<br>Chemical Formula: $NaBH_4$ |
| 8. | N-Methyl 2-pyrolidone (NMP), Qualikem Fine Chemicals Pvt Ltd, Vadodara | Grade A.R, Purity 93 %, Mol. Wt 99.13, Density 1.028g/cc<br>Chemical Formula: $C_5H_9NO$<br>  |

### 4.2.3 Synthesis of *N, N, N*-Trimethyl chitosan chloride

The *N*-methylation reaction of chitosan aiming the preparation of *N, N, N*-trimethyl chitosan chloride was carried out with little modification as described elsewhere [31, 37, 50] as follows: purified chitosan (CHT) 1.0 g (corresponding to 90

m.mol of -$NH_2$) was suspended in NMP (40 ml) in a stainless steel reaction vessel and the suspension was kept at room temperature with constant stirring for 24 h. Then, sodium iodide 2.4 g, aqueous sodium hydroxide (20 %, 10 ml) i.e.2 fold excess of CHT and methyl iodide 5 g i.e. 5 fold excess of CHT (molar concentration, 1g CHT corresponds to 0.913 g. eq. rounded to 1.0 g. eq. of methyl iodide) were added. The vessel was sealed and run for 1h at room temperature on glycerin bath. The temperature was then raised to $50^0$C and treated at this temperature for another 24 h. The clear dark brown liquid so obtained was poured in excess acetone to precipitate out the iodide of trimethyl chitosan. This precipitate was washed 3 to 4 times with acetone. This iodide salt was then subjected to ion exchange by treatment with 50 ml of sodium chloride 10% for 1h. Trimethyl chitosan chloride was then recovered from acetone as above and oven dried at $55^0$C. Sample of different degree of quaternization were also prepared by varying the concentrations of methyl iodide as given Table 4.2. These samples were nomenclatured as TMCHT.

### 4.2.4 Synthesis of *N*-Alkyl and *N*-Aryl chitosan derivatives

The *N*-substitution of chitosan was carried out according to methods described in literature [23, 24, 27]. In general, purified CHT 1g (corresponding to 90 m.mol of -$NH_2$) was dissolved in acetic acid (1%) solution. Required concentration of aqueous aldehyde, listed in Table 4.11, was added gradually to CHT solution at room temperature and stirred for 2 h. The pH of the rection medium was adjusted to 4.5 using few drops of dilute sodium hydroxide solution and then sodium borohydride (10 % aqueous solution) 1.5 fold excess of aldehyde was added very gradually and the stirring was continued for 2h. The precipitate of the *N*-substituted CHT derivative was recovered from alkaline solution at pH 10 by adding sodium hydroxide solution (10%) and then washed thoroughly with distilled water to neutrality. The unreacted aldehyde and other impurities were removed by refluxing with methanol and diethyl ether and then oven dried at $55^0$C. The *N*-substituted CHT derivative was then quaternized with methyl iodide as described in section 4.2.3.

### 4.2.5 Fabric treatment with chitosan and chitosan derivatives by pad-dry cure process

Same method was followed for the application of chitosan derivatives as described in chapter 2, section 2.2.5.

### 4.2.6 Dyeing with direct dyes

Dyeing with direct dyes and the evaluation of colour depth (K/S) and fastness properties were done as described in chapter 2, section 2.2.7.

### 4.2.7 Dyeing with acid dyes

Dyeing with acid dyes and the evaluation of colour depth (K/S) were carried out as described in chapter 2, section 2.2.8.

### 4.2.8 FTIR spectra analysis

FTIR of chitosan and chitosan derivatives were determined using the same method described in chapter 2, section 2.2.11.

### 4.2.9 $^{1}$H-NMR spectra analysis

$^{1}$H-NMR spectra of chitosan and *N*-modified chitosan derivatives were determined using the same method described in chapter 2, section 2.2.12.

### 4.2.10 Elemental analysis

Elemental analysis of CHT and *N*- substituted CHT were carried using the method described in chapter 2, section 2.2.13.

### 4.2.11 Measurement of pH of liquor

The pH of solution was determined using pocket size pH meter (Hanna Instruments, Model HI96107)

### 4.2.12 Conductometric titrations

To determine the degree of quaternization, TMCHT (or quaternized sample) 0.5g was dissolved in water 100 ml containing acetic acid 1ml. The solution was titrated against 0.1M $AgNO_3$ solution conductometrically (Systronics make DDR conductivity meter, model no 304) using platinum electrode cell with cell constant 1.02. The conductance (mMhos) was plotted against burette reading (0.1M $AgNO_3$ solution, ml) to obtain the '*V*' value at lowest conductance. Average of three readings was considered for the calculation. The degree of quaternization (D.Q) can be calculated using following equation.

$$\text{DQ (\%)} = \frac{M_Q \times V \times [AgNO_3]}{m} X100 \qquad \textbf{(4.1)}$$

Where,

$M_Q$ is the molecular weight (g/mol) of repeating unit of TMCHT containing quaternized site, $V$ and [$AgNO_3$] are the equivalent volume and concentration of $AgNO_3$ aqueous solution (0.1M) respectively, and $m$ (g) is the mass of TMCHT.

### 4.2.13 Determination of viscosity

The viscosity of chitosan and chitosan derivatives solutions was measured using the capillary method as described in chapter 2, section 2.2.10.

### 3.2.14 Determination of appearance and stiffness of fabric

Determination of appearance indices and stiffness of fabric samples were done as described in chapter 2, sections 2.2.15 and 2.2.16 respectively.

### 4.2.15 Evaluation of strength loss due to chlorine retention

The strength loss due to chlorine retention was determined according to AATCC Test Method 114-2005. A specified size sample (5 X 5 cm) was treated with sodium hypochlorite solution (1g/L) having 50:1 liquor-to-cloth ratio. The reaction was carried out at room temperature for 15 minutes followed by thorough rinsing and air drying. The

air dried sample was then subjected to steaming under pressure 30psi at 120 $^0$C for 30 minutes. The strength in terms of tenacity (g/tex) of treated and untreated samples was stelometer (SITRA, Coimbator, India) and the strength loss was calculated below formula.

$$\text{Strength loss}(\%) = \frac{A-B}{A} \times 100 \qquad \textbf{(4.2)}$$

Where, A and B are the tenacity (g/tex) of untreated and treated samples respectively.

The loss in whiteness was determined by measuring the yellowness index (2 deg. / C/ ASTM D 1925) on computer colour matching system (Spectroscan 5100A, Premier Colorscan, Mumbai). In order to intensify the yellowness for faster evaluation, the samples were treated with solution containing potassium iodide (10g/L) and acetic acid (10 g/L) for 15 minutes and rinsed. The colour is intensified due to reaction of chloramines with potassium iodide to liberate iodine corresponding to the amount of chlorine retained on fabric [1].

### 4.2.16 Determination of tenacity

The tenacity and elongation of treated and untreated cotton fibres were measured on Stelometer as described in chapter 2, section 2.2.9. The tenacity was calculated using following formula.

$$\text{Tenacity (g/tex)} = \frac{\text{Breaking Load (kgs)} \times 1.5 \times 10}{\text{Sample Weight (mg)}} \qquad \textbf{(4.3)}$$

Sample Length = 1.5 cm

### 4.2.17 Determination of absorbency and crease recovery angle of fabric

Determination of absorbency and crease recovery angles of fabric samples were done as described in chapter 2, sections 2.2.17 and 2.2.18 respectively.

### 4.2.18 Evaluation of soiling behaviour

Soil release properties of CHT and its derivatives treated cotton fabric were evaluated according to AATCC Test Method 151-1990 with little modifications. In brief, a fabric swatch (10 X 10 cm) was treated with standard soil, prepared from vacuum cleaner dirt (100 g) and olive oil (3g), of 80% o.w.m. for 30 minutes in a stainless steel tumble in presence of glass balls (Nos 20, Dia 1.5 cm). The superficial dirt of soil treated sample was then removed by shaking in air and subjected for caging for 15 minutes (twice). The sample was then given soaping treatment at 60 $^0$C for 30 minutes with gentle stirring with 10 g/L detergent (Ezee detergent, Godrej) with liquor to material weight ratio of 50:1 and then rinsed thoroughly and oven dried at 105 $^0$C. The dried samples were preserved in desiccator for 24 hrs, weighed and the amount of soil retained was calculated using following formula.

$$\text{Soil retention}(\%) = \frac{\text{Final Weight (g)} - \text{Initial Weight (g)}}{\text{Initial Weight (g)}} \times 100 \qquad \textbf{(4.4)}$$

The unsoiled and soiled samples were also evaluated on Spectroscan 5100A (Premier Colorscan) for reflectance (% R), K/S values and yellowness index (2 deg / C/ ASTM D 1925) to determine degree of soiling [56, 57] using following expression.

$$\text{Degree of Soiling} = (K/S)_S - (K/S)_U \qquad \textbf{(4.5)}$$

Where, $(K/S)_U$ is the K/S value of unsoiled sample and $(K/S)_S$ that of soiled sample.

### 4.2.19 Soil burial test

The untreated and treated samples were subjected to soil burial test as per AATCC Test Method 30-2004 as described in chapter 2, section 2.2.19.

## 4.3 RESULTS AND DISCUSSION

### 4.3.1 Synthesis and characterization

An objective of the present investigation was in part synthesizing a series of *N*-substituted chitosan derivatives and imparted with quaternary ammonium functionality and then evaluation of their performance on cotton fabric. This was approached by

synthesizing *N*-chitosan derivatives of three categories, viz, trimethyl chitosan chloride, *N*-alkyl substituted quaternized chitosan and *N*-aryl substituted quaternized chitosan.

The main parameters that characterize these chitosan derivatives are degree of substitution (DS) and/or degree of quaternization (DQ). The DQ was determined by conductometric titrations with standard sliver nitrate solution. Instrumental methods like CHN analysis and $^1$HNMR spectroscopy were employed for the quantitative estimation of both DS and DQ. The usefulness of FTIR spectroscopy on *N*-substituted chitosan characterization was mainly employed for qualitative analysis only. Structural modifications of chitosan due to the introduction of methyl and other substituents were characterized by the analysis of FTIR spectra. Viscometry was conducted for the comparative study of aqueous behaviour and molecular weight related properties of these derivatives.

#### *4.3.1.1 Synthesis of N, N, N-trimethyl chitosan chloride*

*N, N, N*-trimethyl chitosan chloride (TMCHT) was synthesized by the treatment of chitosan in *N*-methyl-2-pyrrolidone (NMP) containing sodium iodide and methyl iodide in presence of sodium hydroxide. An anionic exchange of iodide with chloride ion was then followed to get more stable chloride salt as shown in reaction scheme 4.3. The quantities of various ingredients taken for the reaction are enlisted in Table 4.2.

**Table 4.2** Various ingredients used for the synthesis of TMCHT

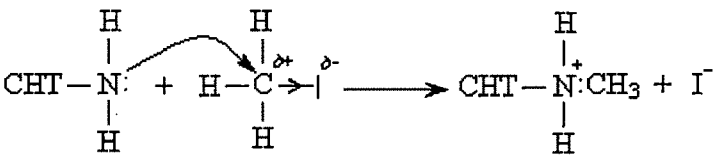
| Sample | Methyl Iodide, g | NMP, ml | CHT:NaOH | CHT:NaI |
|---|---|---|---|---|
| TMCHT1 | 5 | 40 | 1:2 | 1:2.4 |
| TMCHT2 | 10 | 40 | 1:2 | 1:2.4 |
| TMCHT3 | 15 | 40 | 1:2 | 1:2.4 |

*All these concentrations are calculated for 1g CHT*

##### *4.3.1.1.1 Reaction mechanism*

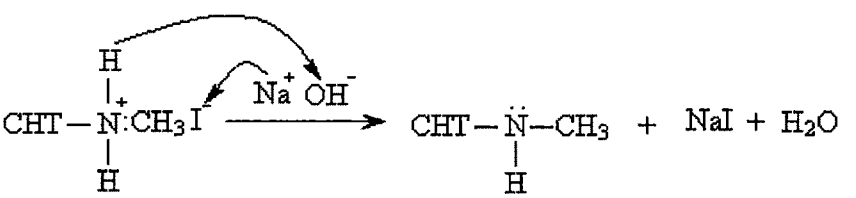
The primary amino groups of chitosan, due to presence of unshared pair of electrons, act as strong nucleophiles (CHT-$N^{\delta-}H_2$). These nucleophiles bond to and yield

products with a variety of electrophiles, so the methylation reaction proceeds via electrophilic substitution.



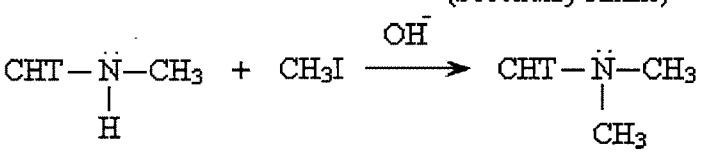
-----(1)

CHT-Nucleophile  Methyl Electrophile  CHT-Methyl cation



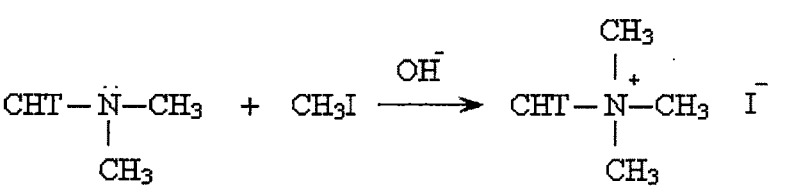
-----(2)

CHT-Methyl cation  N-Methyl CHT (Secondary Amine)



-----(3)

N-Methyl CHT (Secondary amine)  N,N Dimethyl CHT (Tertiary amine)



-----(4)

N,N Dimethyl CHT (Tertiary amine)  N,N,N Trimethyl CHT (Quaternary salt)

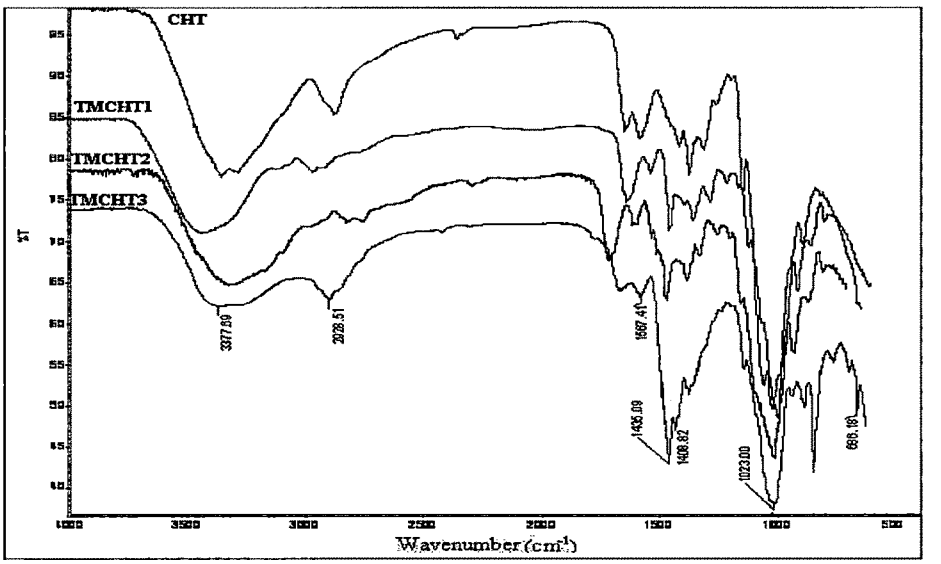
**Scheme 4.5** Electrophilic substitution reaction: Methylation of CHT

In alkyl halides e.g. methyl iodide on the other hand, the electronegative iodine due to induction effect pulls electrons towards it and make the methyl carbon electron deficient

i.e. electrophilic ($H_3C^{\delta+}$–X $^{\delta-}$). The reaction between nucleophilic amines and electrophilic methyl iodide proceeds presumably by a $S_N2$ mechanism and produce methyl chitosan ammonium salt (CHT-Methyl cation). The methyl chitosan ammonium salts in presence of alkali immediately gives secondary amines. The secondary amine undergoes similar reaction with second molecule of methyl iodide to form tertiary amine. The tertiary amine finally reacts with third molecule of methyl iodide to quaternary ammonium salt. Since this reaction system is heterogeneous, a progressive methylation of amines is most probable and possibly gives mixture of mono, di and trimethyl chitosan derivatives [22, 58]. The overall reaction mechanism is illustrated in scheme 4.5.

#### *4.3.1.1.2 FTIR spectra analysis*

The FTIR spectra of CHT and various grades of TMCHT are presented in Figure 4.1. The amino and hydroxyl functional groups in chitosan molecule are characterized by a broad band absorption peak in FTIR spectrum at wavenumber 3355 $cm^{-1}$, which are due to O-H and N-H stretching vibrations. The amino group is characterized by a weak absorption peak at 1585 $cm^{-1}$ due to N-H bending vibrations [59]. Reduction in intensity of these absorption peaks in quaternized chitosan indicates the removal of H of $-NH_2$ groups of chitosan and the formation of new peak at 1470 $cm^{-1}$ corresponds to asymmetrical C-H stretching of methyl ($-CH_3$) group which is introduced through quaternization reaction [18, 23, 59]. With increase in degree of quaternization the intensity of peaks at 3355 and 1585 $cm^{-1}$ in the spectra of TMCHT was decreased progressively with corresponding increase at around 1470 $cm^{-1}$. Thus, the FTIR spectra of synthesized quaternized derivatives of CHT clearly reveal the introduction of methyl groups at nitrogen of glucosamine residues of CHT. When the quaternization was carried out at very high concentration of methyl iodide e.g. 15 fold excess (TMCHT3), another peak (weak) 686 $cm^{-1}$ pertaining to methyl group is also noticed. A small peak appearing at around 1200 $cm^{-1}$ in spectra of all TMCHT may be due to ether linkages. Therefore, the possibility of some methylation at hydroxyl group i.e. *O*-substitution cannot be obviated. Despite the usefulness of FTIR spectroscopy in characterization or qualitative analysis of TMCHT, its application to quantitative determination of DQ is limited due to lack of proportionality between the signals at 1470 $cm^{-1}$ and the DQ.

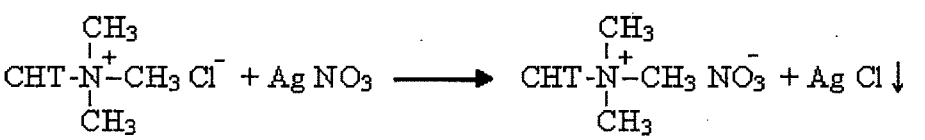



*CHT: Chitosan (Mol wt 135,839), TMCHT1 (CHT:$CH_3I$=1:5), TMCHT2 (CHT: $CH_3I$=1:10), TMCHT3 (CHT: $CH_3I$=1:15)*

**Figure 4.1** FTIR spectra of chitosan and trimethyl chitosan chloride

### *4.3.1.1.3 Conductometric titrations*

Determination of degree of quaternization by conductometric titration [31] is based on the principle that when quaternized chitosan chloride e.g. TMCHT is treated with silver nitrate ($AgNO_3$) solution precipitates out silver chloride as shown by scheme 4.6.




**Scheme 4.6** Reaction of TMCHT chloride with silver nitrate

Above scheme shows that one mole of silver nitrate reacts with equivalent amount of counter chloride ion ($Cl^-$) associated with one quaternized group of glucosamine residue. Thus, the reaction of one mole of silver nitrate with one chloride ion means the reaction with one quaternized group. This reaction, thus, can be employed for the determination of degree of quaternization (DQ) and the amount of $AgNO_3$ consumed can be determined by conductometric titrations.

**Table 4.3** Effect of methyl iodide concentration on DQ: Conductometric titrations readings

| $AgNO_3$ (0.1M) | Conductance (mMhos) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | TMCHT1 CHT:$CH_3I$(1:5) | | | TMCHT2 CHT:$CH_3I$(1:10) | | | TMCHT3 CHT:$CH_3I$(1:15) | | |
| | I | II | III | I | II | III | I | II | III |
| 0 | 3.45 | 3.5 | 3.5 | 3.90 | 3.95 | 3.90 | 3.55 | 3.60 | 3.60 |
| 0.25 | 3.28 | 3.34 | 3.34 | - | - | - | - | - | - |
| 0.5 | 3.10 | 3.16 | 3.18 | 3.85 | 3.80 | 3.85 | 3.40 | 3.40 | 3.40 |
| 0.75 | 2.85 | 3.00 | 3.02 | - | - | - | - | - | - |
| 1.0 | 2.83 | 2.80 | 2.84 | 3.60 | 3.55 | 3.50 | 3.30 | 3.30 | 3.30 |
| 1.25 | 2.64 | 2.7 | 2.64 | - | - | - | - | - | - |
| 1.5 | 2.5 | 2.52 | 2.5 | 3.30 | 3.25 | 3.35 | 3.20 | 3.25 | 3.25 |
| 1.75 | 2.4 | 2.36 | 2.4 | - | - | - | - | - | - |
| 2.0 | 2.2 | 2.2 | 2.2 | 3.20 | 3.20 | 3.25 | 3.05 | 3.10 | 3.10 |
| 2.25 | 2.1 | 2.04 | 2.04 | - | - | - | - | - | - |
| 2.5 | 2.0 | 1.88 | 1.9 | 2.90 | 2.90 | 3.00 | 2.90 | 2.85 | 2.90 |
| 2.75 | 1.93 | 1.8 | 1.8 | - | - | - | - | - | - |
| 3.0 | 2.0 | 1.76 | 2.0 | 2.75 | 2.65 | 2.70 | 2.75 | 2.70 | 2.80 |
| 3.25 | 2.25 | 2.3 | 2.3 | - | - | - | - | - | - |
| 3.5 | 2.52 | 2..4 | 2.66 | 2.50 | 2.55 | 2.60 | 2.70 | 2.70 | 2.75 |
| 3.75 | 2.83 | 2.76 | 2.96 | - | - | - | - | - | - |
| 4.0 | 3.22 | 3.14 | 3.32 | 2.40 | 2.35 | 2.40 | 2.55 | 2.50 | 2.65 |
| 4.25 | 3.35 | 3.4 | 3.6 | - | - | - | - | - | - |
| 4.5 | 3.68 | 3.8 | 3.96 | 2.25 | 2.25 | 2.25 | 2.30 | 2.30 | 2.35 |
| 5.0 | 4.2 | 4.6 | 4.7 | 2.35 | 2.40 | 2.35 | 2.30 | 2.25 | 2.30 |
| 5.5 | - | - | - | - | - | - | 2.15 | 2.10 | 2.20 |
| 6.0 | - | - | - | 3.00 | 3.05 | 3.05 | 2.05 | 2.10 | 2.10 |
| 6.5 | - | - | - | - | - | - | 1.90 | 1.90 | 1.90 |
| 7.0 | - | - | - | 3.75 | 3.65 | 3.70 | 1.75 | 1.70 | 1.75 |
| 7.5 | - | - | - | - | - | - | 1.70 | 1.70 | 1.70 |
| 8.0 | - | - | - | 4.40 | 4.40 | 4.45 | 1.50 | 1.45 | 1.55 |
| 8.5 | - | - | - | - | - | - | 1.50 | 1.50 | 1.50 |
| 9.0 | - | - | - | 5.15 | 5.00 | 5.10 | 1.30 | 1.35 | 1.35 |
| 9.5 | - | - | - | - | - | - | 1.25 | 1.30 | 1.35 |
| 10.0 | - | - | - | 5.75 | 5.70 | 5.75 | 1.20 | 1.30 | 1.25 |
| 10.5 | - | - | - | - | - | - | 1.15 | 1.10 | 1.10 |
| 11.0 | - | - | - | 6.50 | 6.45 | 6.50 | 1.60 | 1.55 | 1.60 |
| 12.0 | - | - | - | 7.25 | 7.20 | 7.25 | 315 | 3.20 | 3.20 |
| 13.0 | - | - | - | - | - | - | 4.50 | 4.55 | 4.50 |
| 14.0 | - | - | - | - | - | - | 6.00 | 5.90 | 5.90 |

*CHT: NaOH (1:2)*

When a standard solution of silver nitrate (0.1M) is added into TMCHT solution, an equivalent amount of AgCl so formed is removed by precipitation resulting into the lowering of conductance. The burette reading at lowest conductance value gives the end point. The average degree of quaternization (DQ) can be calculated by using the expression 4.1.

$$\text{DQ (\%)} = \frac{M_Q \times V \times [AgNO_3]}{m} X100 \qquad \textbf{(4.1)}$$

Where,

$M_Q$ is the molecular weight (g/mol) of repeating unit of TMCHT containing quaternized site, $V$ and [$AgNO_3$] are the equivalent volume and concentration of $AgNO_3$ aqueous solution (0.1M) respectively, and $m$ (g) is the mass of TMCHT.

As for illustration, the burette readings of 0.1M$AgNO_3$ and the corresponding conductance values for TMCHT1, 2 & 3 are presented in Table 4.3 and a representative titration curves shown in Figures 4.2, 4.3 and 4.4. The volume of 0.1M $AgNO_3$ required attaining lowest conductance for all the three TMCHT samples are given in Table 4.4.

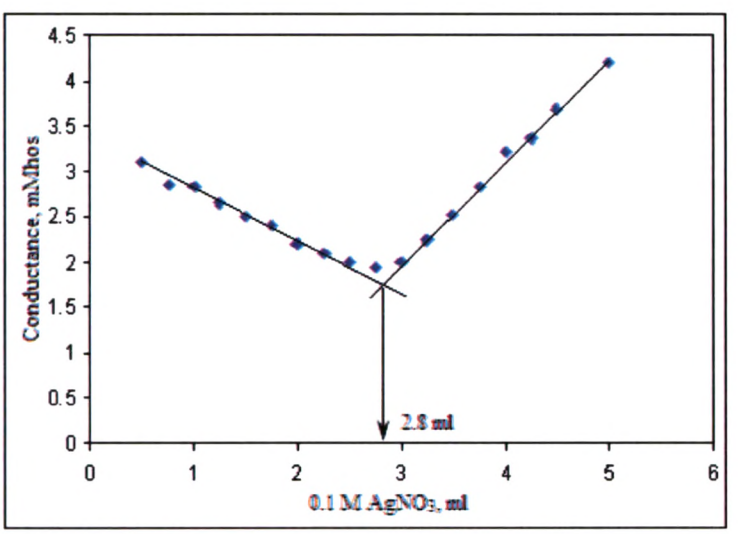



**Figure 4.2** Conductometric titration of TMCHT1 *Vs* $AgNO_3$

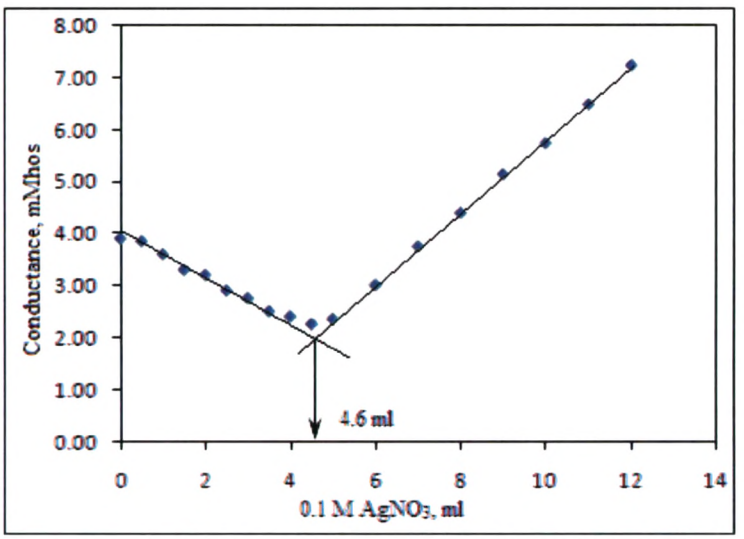



**Figure 4.3** Conductometric titration of TMCHT2 *Vs* $AgNO_3$

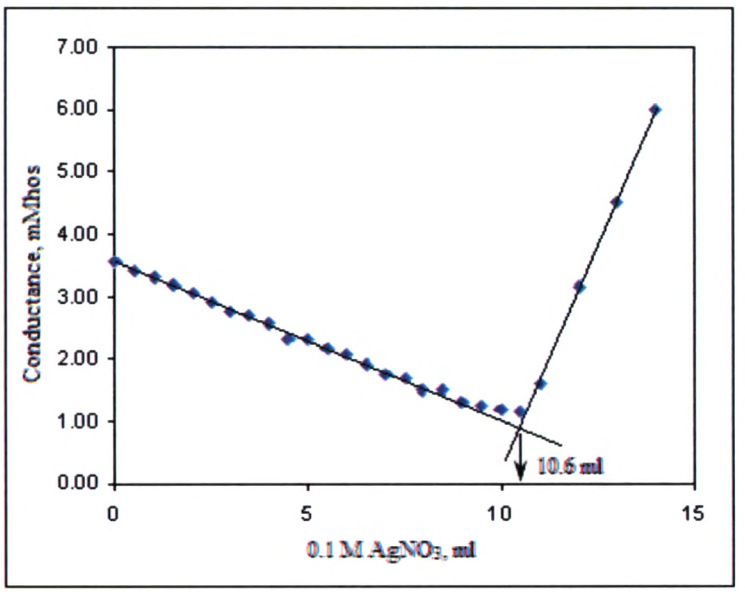



**Figure 4.4** Conductometric titration of TMCHT3 *Vs* $AgNO_3$

**Table 4.4** Conductometric method for determination of degree of quaternization (DQ) of TMCHT

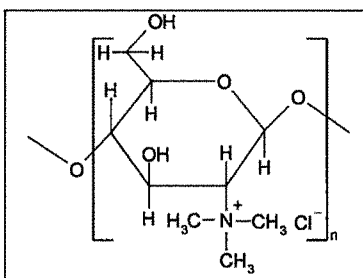
| Sample | 0.1 M $AgNO_3$ titrant (V), ml | | | | Average (DQ), % |
|---|---|---|---|---|---|
| | I | II | III | Average | |
| TMCHT1 | 2.8 | 2.8 | 2.8 | 2.8 | 13.4 |
| TMCHT2 | 4.6 | 4.8 | 4.4 | 4.6 | 22.0 |
| TMCHT3 | 10.6 | 10.8 | 10.5 | 10.63 | 50.9 |

*CHT: NaOH (1:2)*

Calculations:

The degree of quaternization of TMCHT1 is determined as follows:

The molecular weight ($M_Q$) can be calculated from the glucosamine unit containing quaternized site.



| | |
|---|---|
| C,9 X 12 = | 108 |
| O, 4 X 16 = | 64 |
| H, 18 X 1 = | 18 |
| N,1 X 14 = | 14 |
| Cl,1X 35.5= | 35.5 |
| Total, $M_Q$ = | 239.5 |

$M_Q$ = 239.5, m= 0.5 g, [AgNO3] = 0.1M

B.R. = 2.8, 2.8, 2.8 = 2.8 ml i.e. V= 0.0028 L

Substituting these values in the expression 4.1,

$$DQ\ (\%) = \frac{239.5 \times 0.0028 \times 0.1}{0.5} X100 = \mathbf{13.41\%}$$

Similarly, the DQ calculated for TMCHT2 and TMCHT3 are presented in Table 4.4

### *4.3.1.1.4 $^1$HNMR spectroscopy*

The average degree of quaternization of TMCHT is usually determined from the ratio between the intensity (I) of the signal (δ) due to quaternized amino site and the set

of signals attributed to anomeric hydrogen as a reference using the expression 4.6 [20, 31].

$$\text{Degree of Quaternization, DQ (\%)} = \frac{I_{QMe}}{9\left[I_{H1} + I_{H1'}\right]} X100 \qquad \textbf{(4.6)}$$

Where $I_{QMe}$ is integral or intensity due to trimethyl group located at signal δ=3.1 to 3.3 ppm, and, $I_{H1}$ and $I_{H'1}$ represent the integrals of the signals of H1 (the anomeric protons of the D-glucosamine units) and H1' (the anomeric protons of the N-acetyl D- glucosamine units) respectively, at peaks δ= 4.5 to 5.7 ppm. The $^1$HNMR spectrum was determined for TMCHT3 is shown in Figure 4.5.

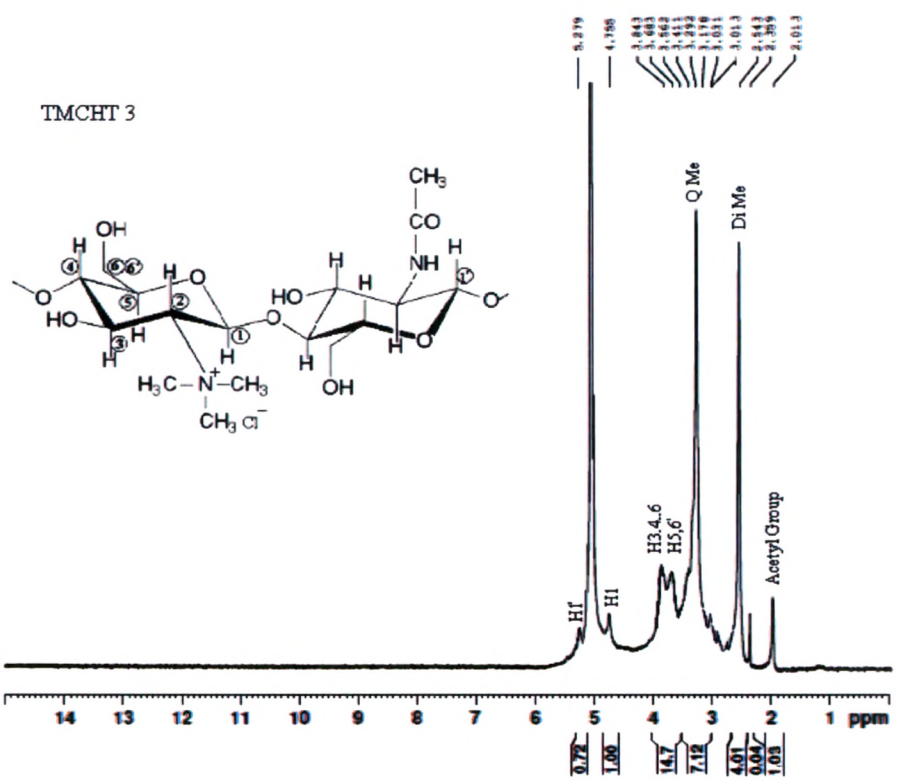



**Figure 4.5** $^1$H NMR spectrum of TMCHT 3

The spectrum indicates that trimethyl group is located at signal δ= 3.292 ppm and the integral was evaluated to be $I_{QMe}$ = 7.12. The integral for anomeric proton H1 at δ= 4. 755 ppm was $I_{H1}$= 1, and that of H1' at δ= 5.279 ppm was found to be $I_{H1'}$= 0.72. The spectrum also shows dimethyl group at δ= 2. 543 ppm and the acetyl group at δ= 2.013 ppm with the corresponding signal intensities $I_{DiMe}$= 4.01 and $I_{NAc}$= 1.03.
Substituting the respective values in expression 4.6,

$$DQ\ (\%) = \frac{I_{QMe}}{9\left[I_{H1} + I_{H1'}\right]} X100 = \frac{7.12}{9\left[1+0.72\right]} X100 = \mathbf{46.0\ \%}$$

The DQ of TMCHT can also be precisely calculated with use of the expression 4.7 [31]. In this case, the denominator of the ratio will be increased as a consequence of the superimposition of signals but much less than in the previous case. In fact, the intensity due to hydrogen bonded to C2 will be added to those of the nine hydrogen atoms of three methyl groups of the quaternized site, six hydrogen atoms of two methyl groups of dimethylated sites and three hydrogen atoms of the methyl group of the acetamido moiety. Thus the impact of superimposition of signals for determination of degree of quaternization (DQ) is relatively much less important in this case.

$$DQ\ (\%) = \frac{I_{QMe}}{9} \times \frac{1}{S} \times 100 \qquad \textbf{(4.7)}$$

$$S = \frac{I_{QMe}}{9} + \frac{I_{DiMe}}{6} + \frac{I_{NAc}}{3} \qquad \textbf{(4.8)}$$

Where,
$I_{QMe}$ and $I_{DiMe}$ correspond, respectively, to the intensities of the signals due to quaternized and dimethylated nitrogen sites present in the chains of TMVRL and $I_{NAc}$ is the signal intensity due to acetyl group. Thus, by computing the equations 4.7 and 4.8 using the integral values from spectrum,

$$S = \frac{I_{QMe}}{9} + \frac{I_{DiMe}}{6} + \frac{I_{NAc}}{3}$$

$$S = \frac{7.12}{9} + \frac{4.01}{6} + \frac{1.03}{3} = 1.8$$

$$DQ\,(\%) = \frac{I_{QMe}}{9} \times \frac{1}{S} \times 100$$

$$DQ\,(\%) = \frac{7.12}{9} \times \frac{1}{1.8} \times 100 = \mathbf{43.9\ \%}$$

These values of degree of quaternization obtained for TMCHT are in close agreement and therefore the average these two i.e. DQ = 44.5 % was taken for the consideration.

#### *4.3.1.1.5 Elemental analysis*

The elemental analysis for carbon, nitrogen, oxygen, hydrogen etc of chitosan and its derivatives can be a useful tool for the characterization i.e. for determination degree of deacetylation (DAC) of chitosan, degree of substitution (DS) by various alkyl and aryl groups or degree of quaternization (DQ) of quaternized chitosan. It is based on the principle that, proportional amount carbon content due to *N*-substitution on chitosan is increased without altering the nitrogen content provided the substituent is free of nitrogen. Thus by comparing the C/N of quaternized chitosan or *N*-substituted chitosan with that of parent chitosan the degree of substitution can be calculated. The expression 4.9 can be employed for such calculations [60].

$$\frac{C1}{N1} \times (1 - DS) + \frac{C2}{N2} \times DS = \frac{C3}{N3} DAC \qquad \textbf{(4.9)}$$

Where, C1/N1 is calculated from the formula of non substituted CHT i.e. glucosamine residue (GlcN), C2/N2 from the N-Substituted residue and C3/N3 is found value of sample by elemental analysis. DAC is degree of deacetylation per unit, which in our case was found to be 0.9.And, DS is degree of substitution of quaternization. The determination of degree of quaternization of TMCHT3 e.g. is illustrated as follows:

The C1/N1 calculated from the formula of non substituted CHT i.e. glucosamine residue (GlcN) is 5.14 and that for C2/N2 from the formula of TMCHT is 7.71. The CHN values of TMCHT3 found by elemental analysis were C3=44.63%, H3=7.07%, N3=6.28 and C3/N3 calculated was 7.11(Table 4.5). The determined C, H and N values of CHT and deferent *N*- modified chitosan derivatives are presented in Table 4.13.

**Table 4.5** Calculations of different C/N ratios of TMCHT

<table>
<tr><td>$\frac{C1}{N1}$</td><td>Calculated from the formula of non substituted CHT i.e.GlcN residue</td><td colspan="4">$\frac{C1}{N1}=\frac{6\times12}{1\times14}=\frac{72}{14}=5.14$</td></tr>
<tr><td>$\frac{C2}{N2}$</td><td>Calculated from the formula of N-Sub residue</td><td colspan="4">$\frac{C2}{N2}=\frac{9\times12}{1\times14}=\frac{108}{14}=7.71$</td></tr>
<tr><td>$\frac{C3}{N3}$</td><td>Values of TMCHT 2 obtained by elemental analysis</td><td>C3 (%)<br>40.19</td><td>H3 (%)<br>7.04</td><td>N3 (%)<br>6.42</td><td>C3/N3<br>6.26</td></tr>
<tr><td>$\frac{C3}{N3}$</td><td>Values of TMCHT 3 obtained by elemental analysis</td><td>C3 (%)<br>44.63</td><td>H3 (%)<br>7.07</td><td>N3 (%)<br>6.28</td><td>C3/N3<br>7.11</td></tr>
</table>

Substituting these values in expression 4.9,

$$\frac{C1}{N1}\times(1-DS)+\frac{C2}{N2}\times DS=\frac{C3}{N3}DAC$$

TMCHT2

$5.14\times(1-DS)+7.71\times DS=6.26\times0.9$

DS = 0.1936 per unit OR **19.4 %**

TMCHT3

$5.14\times(1-DS)+7.71\times DS=7.11\times0.9$

DS = 0.4874 per unit OR **48.7 %**

The results for DQ of different TMCHT determined by various analytical methods namely conductometry, $^1$HNMR and CHN analysis are presented in Table 4.6. It can be observed from the table that exactly same values for DQ are not obtained by different methods employed. Conductometry resulted higher values and somewhat nearer

to elemental analysis. The higher values obtained in conductometry may be attributed to the presence of loose chloride ions that remained with sample even after repeated purification. Further, the possibility of association of chloride ions with mono and di-substituted groups cannot be discarded. Regardless the higher values, the trend observed in conductometry were very much similar with results of elemental analysis.

**Table 4.6** Comparative DQ values of TMCHT determined by various methods

| Sample | DQ values (%) determined by: | | |
|---|---|---|---|
| | Conductometry | $^1$HNMR | C/N Analysis |
| TMCHT1 | 13.4 | - | - |
| TMCHT2 | 22.0 | - | 19.4 |
| TMCHT3 | 50.9 | 44.5 | 48.7 |

***4.3.1.1.6 Effect of reaction conditions on degree of quaternization of TMCHT***

The success or the effectiveness of quaternization of chitosan is anticipated to be influenced by various reaction parameters such as methyl iodide concentration, reaction temperature, duration, process types (single or repeated treatments), and presence of alkali, electrolytes and solvents. The effect of concentration of methyl iodide can be seen from the Table 4.6. It was observed that the DQ increased progressively with increase in concentration of methyl iodide while all other parameters were constant. A sufficiently higher concentration of methyl iodide is always essential for such electrophilic substitution reactions to occur in heterogeneous medium. By increasing the reaction time or by repeated methylation process, increased DQ of chitosan has been reported earlier [19] but with the adverse effect on intrinsic viscosity and hence the molecular weight.

The mechanism of electrophilic substitution reaction proposed for the methylation of CHT in scheme 4.5 shows the indispensability of alkali in the reaction mixture. Accordingly, the effect of sodium hydroxide concentration on DQ of 1g CHT was studied. The methylation was carried out with methyl iodide (15 fold excess) and the caustic concentration was varied from zero concentration to 4 fold excess of CHT. The readings are given in Table 4.7, Table 4.8 and Table 4.9. The DQ was determined by conductometry are given in Table 4.10. These results reveal that the degree of

quaternization was almost nil in absence of alkali and then increased with increase in concentration of sodium hydroxide. Very high concentrations of sodium hydroxide, however, seemed to be detrimental on the quaternization efficiency. Further, incorporation of co-solvent such as NMP improved the degree of quaternization.

**Table 4.7** Conductometric titration readings for TMCHT prepared in absence of sodium hydroxide

| $AgNO_3$ (0.1M) | Conductance, mMhos | | |
|---|---|---|---|
| | I | II | III |
| 0 | 3.70 | 3.85 | 3.65 |
| 0.25 | 3.20 | 1.55 | 3.35 |
| 0.50 | 3.55 | 3.34 | 3.70 |
| 0.75 | 4.05 | 3.73 | 4.05 |
| 1.00 | 4.45 | 4.05 | 4.40 |
| 1.25 | 4.90 | 4.40 | 4.80 |
| 1.50 | 5.35 | 4.90 | 5.25 |
| 1.75 | 5.75 | 5.20 | 5.65 |
| 2.00 | 0.00 | 5.40 | 0.00 |
| 2.25 | 6.45 | 6.00 | 6.45 |
| 2.50 | 6.85 | 6.35 | 6.85 |

*CHT: $CH_3I$=1:15, NMP 40ml*

The poor quaternization yield in absence of alkali in quaternization reaction of chitosan can be explained on the fact that the CHT-Methyl cations intermediates formed during methylation (Scheme 4.5, step 1) liberate protons ($H^+$) as a by-product, as shown in scheme 4.7. The liberated protons being highly electrophilic in nature are captured by unshared electron pair of the nitrogen and thus stop the reaction at the amino site or preclude the forward reaction. Further, the low pH causes chain depolymerization due to glycoside bond cleavage, yielding low molecular weight derivatives [10]. These problems can be overcome by addition of strong bases that can remove the liberated H+ and favor the forward reaction. Different types of bases both organic (triethylamine) and inorganic (NaOH) can be employed in quaternization of CHT [61]. Studies have demonstrated that the inorganic bases were more efficient than organic bases due to their strong nucleophilic character. NaOH, for example, has a larger pKa than chitosan for

neutralizing the hydroiodic acid produced during the reaction and therefore avoids the protonation of the unreacted $NH_2$ groups [17].

**Table 4.8** Effect of sodium hydroxide on DQ of TMCHT: Conductometric titrations readings

| $AgNO_3$ (0.1M) | Conductance (mMhos) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | CHT: NaOH (1:1) (With NMP) | | | CHT: NaOH (1:2) (Without NMP) | | | CHT :NaOH (1:2) (With NMP) | | |
| | I | II | III | I | II | III | I | II | III |
| 0 | 3.80 | 3.80 | 3.80 | 3.70 | 3.60 | 3.70 | 3.55 | 3.60 | 3.60 |
| 0.5 | 3.75 | 3.65 | 3.70 | 3.60 | 3.60 | 3.65 | 3.40 | 3.40 | 3.40 |
| 1.0 | 3.60 | 3.50 | 3.50 | 3.50 | 3.40 | 3.40 | 3.30 | 3.30 | 3.30 |
| 1.5 | 3.40 | 3.35 | 3.50 | 3.25 | 3.25 | 3.30 | 3.20 | 3.25 | 3.25 |
| 2.0 | 3.25 | 3.20 | 3.20 | 3.20 | 3.20 | 3.25 | 3.05 | 3.10 | 3.10 |
| 2.5 | 3.00 | 3.00 | 3.00 | 3.10 | 3.10 | 3.10 | 2.90 | 2.85 | 2.90 |
| 3.0 | 2.80 | 2.90 | 2.90 | 2.90 | 2.85 | 2.85 | 2.75 | 2.70 | 2.80 |
| 3.5 | 2.60 | 2.70 | 2.60 | 2.80 | 2.75 | 2.75 | 2.70 | 2.70 | 2.75 |
| 4.0 | 2.50 | 2.55 | 2.55 | 2.75 | 2.75 | 2.65 | 2.55 | 2.50 | 2.65 |
| 4.5 | 2.30 | 2.35 | 2.30 | 2.50 | 2.55 | 2.55 | 2.30 | 2.30 | 2.35 |
| 5.0 | 2.10 | 2.15 | 2.20 | 2.45 | 2.50 | 2.50 | 2.30 | 2.25 | 2.30 |
| 5.5 | 1.90 | 1.85 | 1.90 | 2.40 | 2.35 | 2.35 | 2.15 | 2.10 | 2.20 |
| 6.0 | 1.80 | 1.85 | 1.85 | 2.25 | 2.30 | 2.30 | 2.05 | 2.10 | 2.10 |
| 6.5 | 1.60 | 1.65 | 1.65 | 2.30 | 2.25 | 2.30 | 1.90 | 1.90 | 1.90 |
| 7.0 | 1.40 | 1.45 | 1.50 | 2.25 | 2.20 | 2.20 | 1.75 | 1.70 | 1.75 |
| 7.5 | 1.35 | 1.30 | 1.35 | 2.35 | 2.35 | 2.35 | 1.70 | 1.70 | 1.70 |
| 8.0 | 1.30 | 1.35 | 1.30 | 2.75 | 2.80 | 2.75 | 1.50 | 1.45 | 1.55 |
| 8.5 | 1.45 | 1.50 | 1.55 | 3.50 | 3.50 | 3.50 | 1.50 | 1.50 | 1.50 |
| 9.0 | 2.00 | 2.05 | 2.05 | 2.40 | 2.35 | 2.35 | 1.30 | 1.35 | 1.35 |
| 9.5 | - | - | - | - | - | - | 1.25 | 1.30 | 1.35 |
| 10.0 | 3.05 | 3.00 | 3.00 | 4.25 | 4.20 | 4.20 | 1.20 | 1.30 | 1.25 |
| 10.5 | - | - | - | - | - | - | 1.15 | 1.10 | 1.10 |
| 11.0 | 3.95 | 4.00 | 4.00 | 5.25 | 5.20 | 5.25 | 1.60 | 1.55 | 1.60 |
| 12.0 | 5.00 | 4.90 | 4.90 | 6.15 | 6.20 | 6.15 | 315 | 3.20 | 3.20 |
| 13.0 | 6.15 | 6.00 | 6.20 | 6.60 | 6.65 | 6.65 | 4.50 | 4.55 | 4.50 |
| 14.0 | 6.80 | 6.80 | 6.85 | 7.00 | 6.90 | 6.90 | 6.00 | 5.90 | 5.90 |

*CHT: $CH_3I$ =1:15, NMP 40ml*

**Table 4.9** Effect of sodium hydroxide on DQ of TMCHT: Conductometric titrations readings

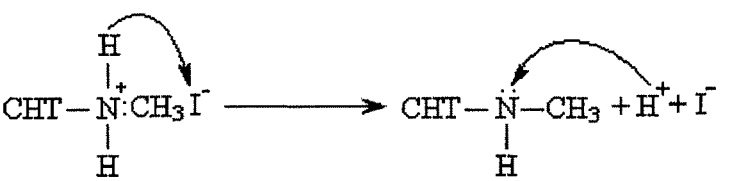
| $AgNO_3$ (0.1M) | Conductance, mMhos | | | | | |
|---|---|---|---|---|---|---|
| | CHT: NaOH (1:3) | | | CHT: NaOH (1:4) | | |
| | I | II | III | I | II | III |
| 0 | 3.95 | 3.90 | 3.95 | 3.65 | 3.60 | 3.70 |
| 0.5 | 3.85 | 3.85 | 3.85 | 3.55 | 3.60 | 3.60 |
| 1.0 | 3.65 | 3.70 | 3.70 | 3.45 | 3.40 | 3.45 |
| 1.5 | 3.50 | 3.50 | 3.60 | 3.25 | 3.30 | 3.25 |
| 2.0 | 3.40 | 3.35 | 3.50 | 3.10 | 3.15 | 3.10 |
| 2.5 | 3.25 | 3.25 | 3.30 | 3.00 | 3.10 | 3.00 |
| 3.0 | 3.00 | 3.10 | 3.10 | 2.75 | 2.80 | 2.90 |
| 3.5 | 3.85 | 3.80 | 2.90 | 2.70 | 2.75 | 2.75 |
| 4.0 | 2.75 | 2.80 | 2.80 | 2.55 | 2.60 | 2.60 |
| 4.5 | 2.65 | 2.70 | 2.70 | 2.50 | 2.45 | 2.55 |
| 5.0 | 2.50 | 2.45 | 2.50 | 2.25 | 2.30 | 2.20 |
| 5.5 | 2.30 | 2.25 | 2.35 | 2.10 | 2.20 | 2.20 |
| 6.0 | 2.25 | 2.20 | 2.30 | 2.00 | 2.10 | 2.05 |
| 6.5 | 2.00 | 2.10 | 2.05 | 1.85 | 1.80 | 1.80 |
| 7.0 | 1.90 | 1.90 | 1.90 | 1.75 | 1.75 | 1.80 |
| 7.5 | 1.75 | 1.80 | 1.80 | 1.60 | 1.70 | 1.65 |
| 8.0 | 1.60 | 1.55 | 1.60 | 1.50 | 1.50 | 1.55 |
| 8.5 | 1.55 | 1.55 | 1.55 | 1.40 | 1.40 | 1.45 |
| 9.0 | 1.35 | 1.35 | 1.40 | 1.35 | 1.35 | 1.40 |
| 9.5 | 1.25 | 1.30 | 1.30 | 1.50 | 1.50 | 1.55 |
| 10.0 | 1.20 | 1.20 | 1.20 | 2.25 | 2.30 | 2.20 |
| 10.5 | 1.40 | 1.35 | 1.35 | - | - | - |
| 11.0 | 2.00 | 2.00 | 2.05 | 3.50 | 3.50 | 3.60 |
| 12.0 | 3.25 | 3.25 | 3.20 | 4.75 | 4.70 | 4.80 |
| 13.0 | 4.50 | 4.45 | 4.50 | 6.00 | 6.00 | 6.10 |
| 14.0 | 5.70 | 5.60 | 5.60 | 7.30 | 7.25 | 7.40 |
| 15.0 | 7.00 | 6.90 | 6.90 | - | - | - |
| 16.0 | 8.00 | 8.10 | 8.10 | - | - | - |

*CHT: $CH_3I$=1:15, NMP 40ml*

**Table 4.10** Effect of sodium hydroxide on DQ of TMCHT

| CHT: NaOH | $AgNO_3$(0.1M), ml | | | | NMP, ml | DQ, % |
|---|---|---|---|---|---|---|
| | I | II | III | Average | | |
| 1:0 | 0.25 | 0.5 | 0.25 | 0.33 | 40 | 1.6 |
| 1:1 | 8.00 | 7.90 | 8.05 | 7.98 | 40 | 38.32 |
| 1:2 | 6.90 | 6.90 | 6.90 | 6.90 | - | 33.05 |
| 1:2 | 10.60 | 10.80 | 10.50 | 10.63 | 40 | 50.92 |
| 1:3 | 10.10 | 10.10 | 10.00 | 10.06 | 40 | 48.17 |
| 1:4 | 9.30 | 9.30 | 9.40 | 9.33 | 40 | 44.68 |

*CHT: $CH_3I$ =1:15*



CHT-Methyl cation

N-Methyl CHT
(Secondary amine)

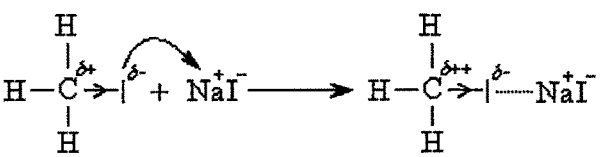
**Scheme 4.7** Proton liberation step in methylation of CHT

Higher concentrations of alkali, on the other hand, may lead to side reactions. The nucleophilic $OH^-$ of the added NaOH can react with the electrophile ($CH_3I$) and produces alcohols ($CH_3OH$) as shown in scheme 4.8. Excessively higher concentrations of alkali may also lead to *O*-substitution to produce 3-*O*-methyl and 6-*O*-methyl derivatives [16, 62], which may cause steric hindrance for alkylation on amino groups. Overall effect will be lesser methylation on amino nitrogen.

**Scheme 4.8** Side reaction due to alkali

The highly compact structure of chitosan due to extensive intramolecular and intermolecular hydrogen bonding between the chains confer it insolubility in neutral

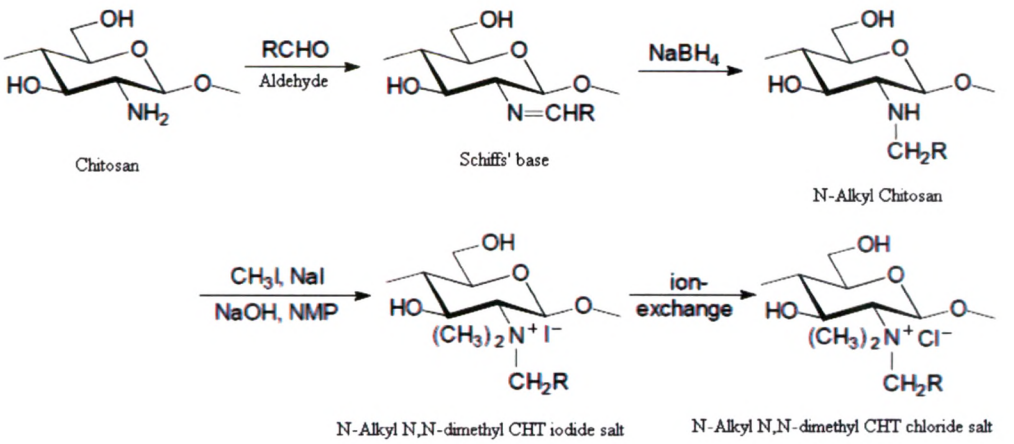
conditions. Since the quaternization reaction is performed in alkaline medium, the system is heterogeneous. This offers greater resistance for the penetration of methyl iodide and sodium hydroxide into the CHT structure and results into the poor degree of quaternization. Treatment of highly polar co-solvent such as *N*-methyl-2-pyrrolidone (other examples are DMF, DMSO etc) with CHT for an ample dwell time prior to the addition of methyl iodide and NaOH can swell and open up the CHT particles and facilitate the greater penetration alkylating chemicals [13]. The reaction speed and degree of methylation can also be increased by increasing temperature. However higher temperatures have been found to lead O-alkylation and also caused degradation of the chitosan as reported by Kotze et al [62]. Therefore, the same optimal temperature $50^0$C and the sodium iodide concentration, as published elsewhere [31,37, 50], was adapted. Use of sodium iodide was reported to be necessary to adjust the overall concentration of reactants in the reaction medium [37]. It is believed that sodium iodide in reaction bath interacts with methyl iodide through ion- dipole forces and enhances the compatibility with the medium [22]. This interaction is also believed to make methyl carbon more electrophilic due to pulling of electronegative iodine of methyl iodide towards sodium ion of NaI and thus favor the methylation faster. The probable role of sodium iodide in methylation reaction is illustrated in scheme 4.9.



**Scheme 4.9** Reaction of sodium iodide with methyl iodide

### *4.3.1.2 Synthesis of N-alkyl N, N-dimethyl chitosan chloride*

In order to synthesize chitosan derivatives with quaternary ammonium salt having different methylene spacers a two step protocol was followed in which the first step involved synthesizing the *N*-alkyl derivatives of chitosan with varying degrees of hydrophobic character. In second step, these derivatives were subjected to quaternization to obtain targeted compounds.




**Scheme 4.10** Synthesis *N*-alkyl *N,N*-dimethyl chitosan chloride

**Table 4.11** Various ingredients used in the synthesis of *N*-sub CHT

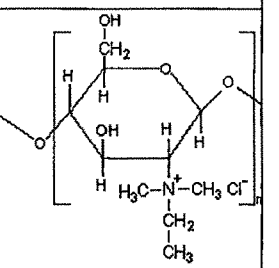
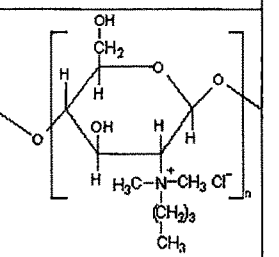
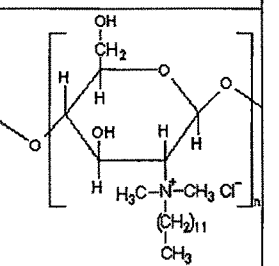
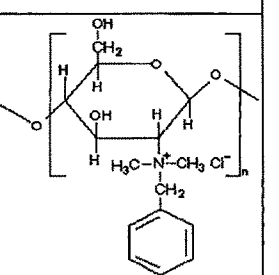
| Sample | Aldehyde | *Aldehyde concentration | | $NaBH_4$, g |
|---|---|---|---|---|
| | | Relative to CHT | Quantity, g | |
| N-Et CHT(1:2) | Acetaldehyde | Two fold excess | 0.6 | 1.0 |
| N-Et CHT(1:4) | Acetaldehyde | Four fold excess | 1.2 | 2.0 |
| N-Bu CHT(1:2) | n-Butyraldehyde | Two fold excess | 1.0 | 1.5 |
| N-Bu CHT(1:4) | n-Butyraldehyde | Four fold excess | 2.0 | 3.0 |
| N-DodCHT(1:2) | Dodecyl Aldehyde | Two fold excess | 2.4 | 3.6 |
| N-DodCHT(1:4) | Dodecyl Aldehyde | Four fold excess | 4.8 | 7.2 |
| N-Bz CHT(1:2) | Benzaldehyde | Two fold excess | 1.4 | 2.1 |
| N-Bz CHT(1:4) | Benzaldehyde | Four fold excess | 2.8 | 4.2 |
| N-Np CHT(1:2) | 1-Napthaldehyde | Two fold excess | 2.0 | 3.0 |
| N-Np CHT(1:4) | 1-Napthaldehyde | Four fold excess | 4.0 | 3.0 |

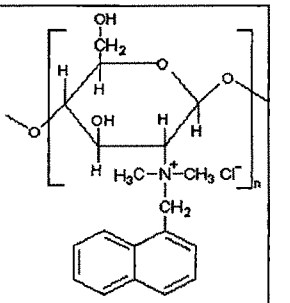
*CHT 1 g, [*Conc calculated for aldehyde was based on molar conc in g. eq of -$NH_2$ of CHT. Calculation for two fold excess of acetaldehyde concentration can be illustrated as follows: 1g of CHT corresponds to 90 m.mol of $NH_2$ which in turn corresponds to 283 m.mol of acetaldehyde. That means 1g CHT contains 0.09 g eq of -$NH_2$ groups and reacts with acetaldehyde 0.283g (~ 0.3g). Therefore, for two fold excess, the quantity of pure acetaldehyde will be 0.3 X 2= 0.6 g.*]

Three alkyl groups of different chain length namely ethyl, butyl and dodecyl groups were, therefore, selected for the present study. These groups were introduced by reacting respective aldehyde, as listed in Table 4.11, with CHT in acidic medium to form Schiff's base. These intermediates were subjected to reductive amination known as Bosch reduction using sodium borohydride to produce *N*-alkyl derivatives. *N*-alkyl CHT

derivatives were further quaternized with methyl iodide as described in text for TMCHT (Scheme 4.10). The quaternization process for all these *N*-substituted CHT was carried out with methyl iodide of fifteen fold excess concentration. Different grades of *N*-alkyl CHT and *N*-alkyl *N, N*-dimethyl chitosan chloride derivatives synthesized for textile application are listed in Table 4.12.

**Table 4.12** Various *N*-substituted CHT derivatives

| **Code** | **Chemical Name** | **Structure of quaternized derivative** |
|---|---|---|
| N-Et CHT(1:2) | N-Ethyl Chitosan (1:2) |  |
| N-Et CHT(1:4) | N-Ethyl Chitosan (1:4) | |
| N-Et Q CHT(1:2) | N-Ethyl N,N Dimethyl Chitosan (1:2) Chloride | |
| N-Et Q CHT(1:4) | N-Ethyl N,N Dimethyl Chitosan (1:4) Chloride | |
| N-Bu CHT(1:2) | N-Butyl Chitosan (1:2) |  |
| N-Bu CHT(1:4) | N-Butyl Chitosan (1:4) | |
| N-Bu Q.CHT(1:2) | N-Butyl N,N Dimethyl Chitosan (1:2) Chloride | |
| N-Bu Q.CHT(1:4) | N-Butyl N,N Dimethyl Chitosan (1:4) Chloride | |
| N-DodCHT(1:2) | N-Dodecyl Chitosan (1:2) |  |
| N-DodCHT(1:4) | N-Dodecyl Chitosan (1:4) | |
| N-DodQ.CHT(1:2) | N- Dodecyl N,N Dimethyl Chitosan (1:2) Chloride | |
| N-DodQ.CHT(1:4) | N- Dodecyl N,N Dimethyl Chitosan (1:4) Chloride | |
| N-Bz CHT(1:2) | N-Benzyl Chitosan (1:2) |  |
| N-Bz CHT(1:4) | N-Benzyl Chitosan (1:4) | |
| N-Bz Q.CHT(1:2) | N-Benzyl N,N Dimethyl Chitosan (1:2) Chloride | |
| N-Bz Q.CHT(1:4) | N-Benzyl N,N Dimethyl Chitosan (1:4) Chloride | |

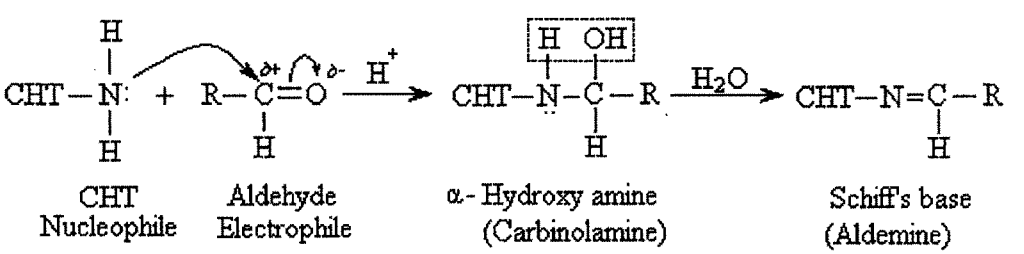
| | | |
|---|---|---|
| N-Np CHT(1:2) | N-(1-Naphthyl) Methylene Chitosan (1:2) |  |
| N-Np CHT(1:4) | N-(1-Naphthyl) Methylene Chitosan (1:4) | |
| N-Np Q.CHT(1:2) | N-(1-Naphthyl) Methylene N,N Dimethyl Chitosan (1:2) Chloride | |
| N-Np Q.CHT(1:4) | N-(1-Naphthyl) Methylene N,N Dimethyl Chitosan (1:4) Chloride | |

*CHT: $CH_3I$ =1:15, Values in parenthesis indicate CHT: Aldehyde ratio*

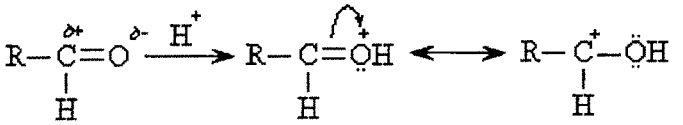
#### *4.3.1.2.1 Reaction mechanism*

The primary amines of chitosan (CHT) readily add to the carbonyl group (>C=O) of aldehydes to form α- hydroxy amines, also called carbinolamines. These species undergo spontaneous elimination of water molecule to yield imines or Schiff's base [22]. This is an electrophilic substitution reaction and follows $S_N2$ mechanism. The carbon-oxygen bond in carbonyl group of aldehydes is highly polarized due to the presence of electro-ve oxygen. The electrons constituting the π bonds are partially shifted towards oxygen as a result of electromeric effect. It implies that the carbon atom of carbonyl group is electron deficient i.e. electrophile and therefore readily attacks nucleophilic amino group of CHT.

The acidic pH in this reaction serves two purposes. Firstly, it promotes the dissolution of chitosan conferring the homogeneity to the reaction medium. Secondly, it acts as a catalyst. The proton released by the acid combines with the carbonyl oxygen and thus attenuates the electron deficiency of the carbon atom and thus the attack of nucleophile is enhanced. The various steps of the reaction mechanism are shown in scheme 4.11.

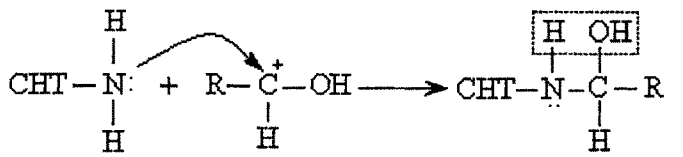



(1)



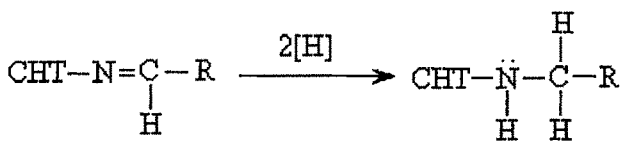
(2)

Acid catalyzed reaction , protonation of aldehyde



(3)

CHT (Nucleophile) Protonated aldehyde (Electrophile) α- Hydroxy amine (Carbinolamine)



(4)

Schiff's base N-Alkyl CHT (Secondary amine)

Reduction of Schiff's base (Bosch reduction)

**Scheme 4.11** Electrophilic substitution reaction: methylation of CHT

#### *4.3.1.2.2 FTIR spectroscopy of N-alkylated chitosans*

The FTIR spectra of different *N*-alkylated and quaternized *N*-alkylated chitosan are presented in Figures 4.6, 4.7 and 4.8. The FTIR spectrum of N-ethyl chitosan (Figures 4.6) shows a reduction in broad band at 3372 $cm^{-1}$ that indicates the removal of some of H from $NH_2$. A characteristic peak at wavenumber 2928 $cm^{-1}$ arised is mainly due to C-H stretching due to the introduction of methylene group. The intensities of these peaks were found to be increased with increase in methylene spacer as is observed in Figures 4.7 and 4.8. The terminal methyl group of attached ethyl chain is also recognized by a weak absorption peak at 1457 $cm^{-1}$ due to C-H bending vibrations. Although marked differences were not observed in FTIR spectra for the quaternized chitosan, the intensity at peak around 1457 $cm^{-1}$ was found to be increased which is the characteristic peak of methyl group [16, 23].

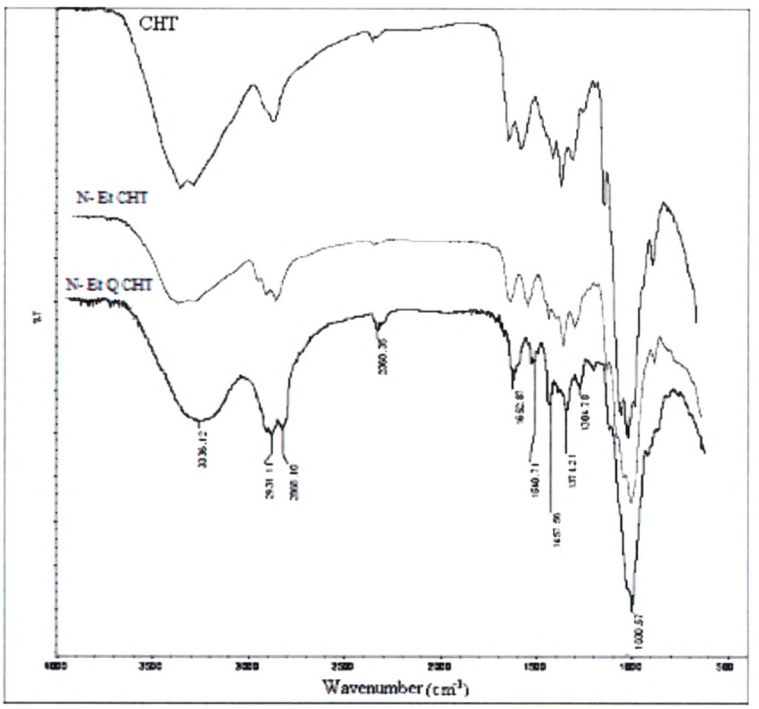



**Figure 4.6** FTIR spectra of *N*- ethyl chitosan derivatives

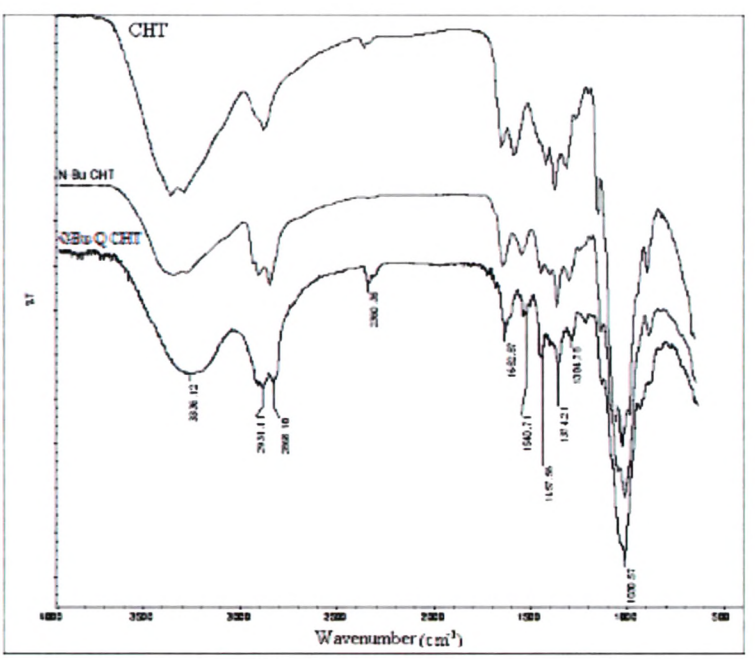



**Figure 4.7** FTIR spectra of *N*-butyl chitosan derivatives

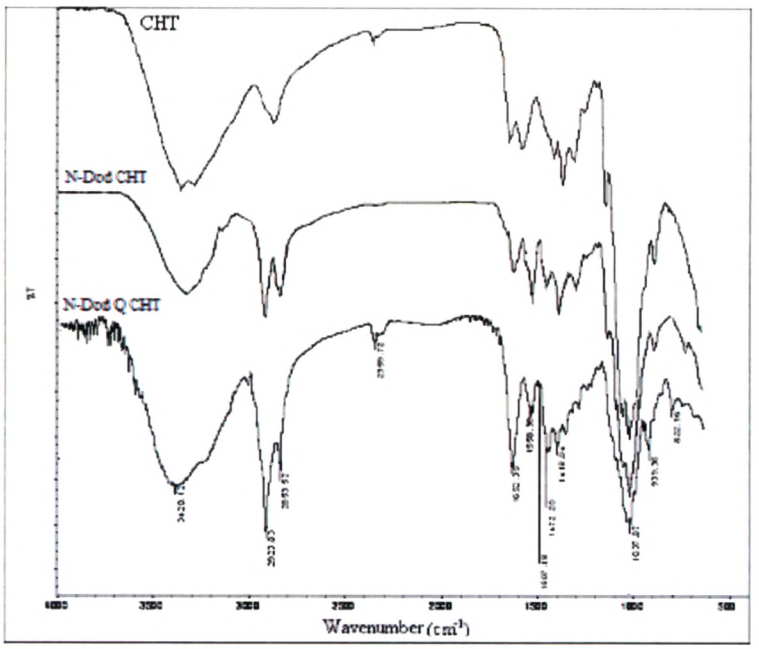



**Figure 4.8** FTIR spectra of *N*-dodecyl chitosan derivatives

#### *4.3.1.2.3 Analysis of $^1$HNMR spectra of N-alkylated chitosans*

The $^1$HNMR spectroscopy was performed for the quantitative determination of degree of substitution (DS) and degree of quaternization (DQ) of synthesized *N*-alkyl CHT and their quaternized derivatives. The degree of substitution from the $^1$HNMR spectrum can be calculated from the ratio of intensities produced due to proton vibration / resonance from C-H bond of substituent to that of either C2 proton or the sum of anomeric protons. In present study, the degree of substitution (DS) was calculated using two different equations 4.10 [28] and 4.11 [24, 25] and the average of these two results was considered. The spectra of these derivatives are shown in Figures 4.9 to 4.14. The values of these parameters determined for *N*-alkyl CHT and their quaternized derivatives are presented in Table 4.19. The $^1$H-NMR spectrum of modified chitosan displays broadening of the characteristic peaks at signals in the 1.7-0.9 ppm region, attributed to the protons of the methyl (-$CH_3$) and methylene (-CH2-) groups grafted onto the chitosan chain, which evidences the chemical modifications resulting from the alkylation reaction. The broad multiplet peaks from 1.3 to 1.7 ppm are attributed to the methylene hydrogen of the -$CH_2$- groups, while a typical peak at 0.9 ppm corresponds to the methyl protons at the terminal groups -$CH_3$, both belonging to the -$C_2H_5$ aliphatic chain [13, 63- 65]. The

degree of quaternization of the quaternized *N*-alkylated samples was determined using the equation 4.6 with little modification.

### *$^1$NMR spectrum analysis of N- ethyl chitosan [N- Et CHT (1:2)]*

The $^1$HNMR spectrum of the *N*-Et CHT (1:2) prepared from two fold excess of acetaldehyde is shown in Figure 4.9. In the figure, the peak at δ= 1.019 ppm is attributed to terminal methyl group of pendant ethyl chain and the integral is $I_{Me\ (T)} = 2.82$ and the signal at δ= 1.323 ppm is assigned to -CH2- of ethyl chain with integral $I_{(-CH2-)} = 1.47$. This figure also depicts the acetyl group at δ= 1.960 with integral $I_{NAc}$= 1.0, and protons at C2,3,4,5,6 & 6' between range of δ= 3 to 4 ppm with total intensity $I_{H3\text{-}6,6'} = 7.22$ . The C2 proton was traced at peak $\delta_{(H2)} = 2.854$ with integral the $I_{H2} = 3.78$. The anomeric protons H1 and H1' are traced at δ= 4.601ppm and δ= 5.433 ppm respectively and the corresponding integrals are found to be $I_{H1}$= 1 and $I_{H1'}$= 0.66.

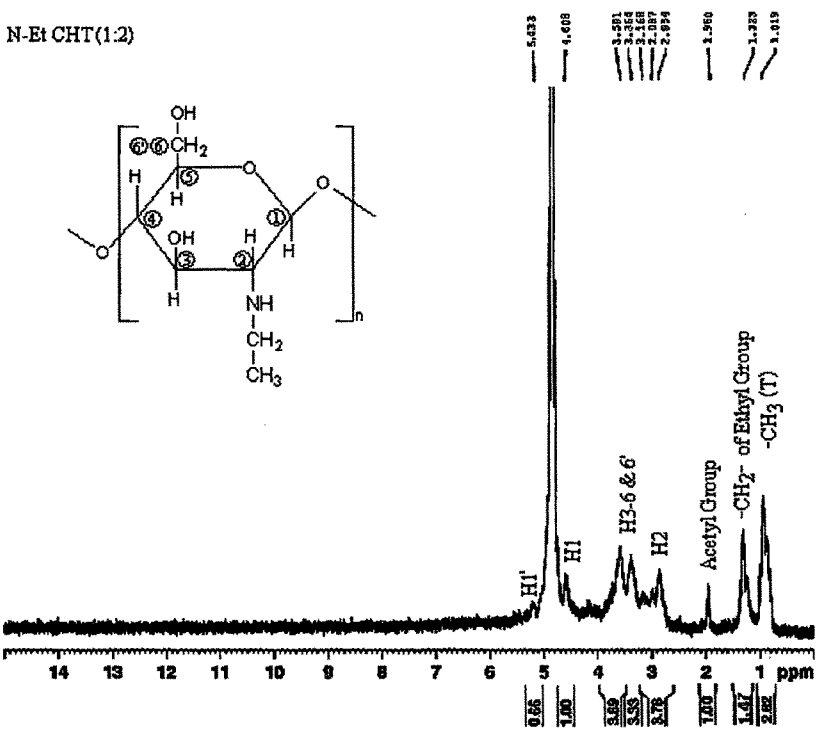



**Figure 4.9** $^1$HNMR spectrum of N-Ethyl chitosan (1:2)

Calculations:

Method1: The degree of substitution (DS, %) can be calculated by substituting the values of integrals in equation 4.10

$$DS(\%) = \frac{I_{(-CH2-)}}{2\left[I_{H1} + I_{H1'}\right]} X100 \qquad \textbf{(4.10)}$$

$$= \frac{1.47}{2\left[1+0.66\right]} X100 = \textbf{44.3 \%}$$

Method 2:

$$\frac{nDS}{6} = \frac{A}{\left[B+C\right]} \quad \textbf{OR} \quad \frac{nDS}{6} = \frac{I_{Et}}{\left[I_{H2} + I_{H3\text{-}6,6'}\right]} \qquad \textbf{(4.11)}$$

Where, A = Peak area of substituent.

Therefore, A= $I_{Et} = I_{Me} + I_{-CH2-} = 2.82 + 1.47 = 4.29$

B = Peak area of H2 (proton at C2) of glucosamine residue ( Glc N).

i.e. B = $I_{H2}$ = 3.78 at δ= 2.854ppm for proton at C2 of GlcN.

C = Peak area of protons bounded to C-3,4,5,6& 6' of GlcN.

C = $I_{H3\text{-}6\&6'} = 3.33 + 3.89 = 7.22$ (at δ= 3.168 and 3.581ppm)

n= Number of proton per substituent $-CH_2-CH_3 = 5$

The denominator '6' at LHS is the total number of protons bound to C2 of GlcN and C3-6&6' ie.[B+C] or [H2+ H3,4,5,6& 6'].

By substituting above values in equation **4.11,**

$$DS = \frac{6 \times 7.49}{5 \times \left[3.78 + 3.33 + 3.89\right]} = 0.468 \text{ ethyl groups/glucosamine unit.}$$

**DS (%) = 46.8 %**

Average of method 1 and method 2, **DS = 45.5 %**

***[1]NMR Spectrum Analysis of N- Ethyl N, N-dimethyl chitosan chloride (1:2) [N-Et Q CHT(1:2)]***

The [1]HNMR spectrum of N- Ethyl N, N-dimethyl chitosan chloride (1:2) [N-Et Q CHT(1:2)] is shown in Figure 4.10.

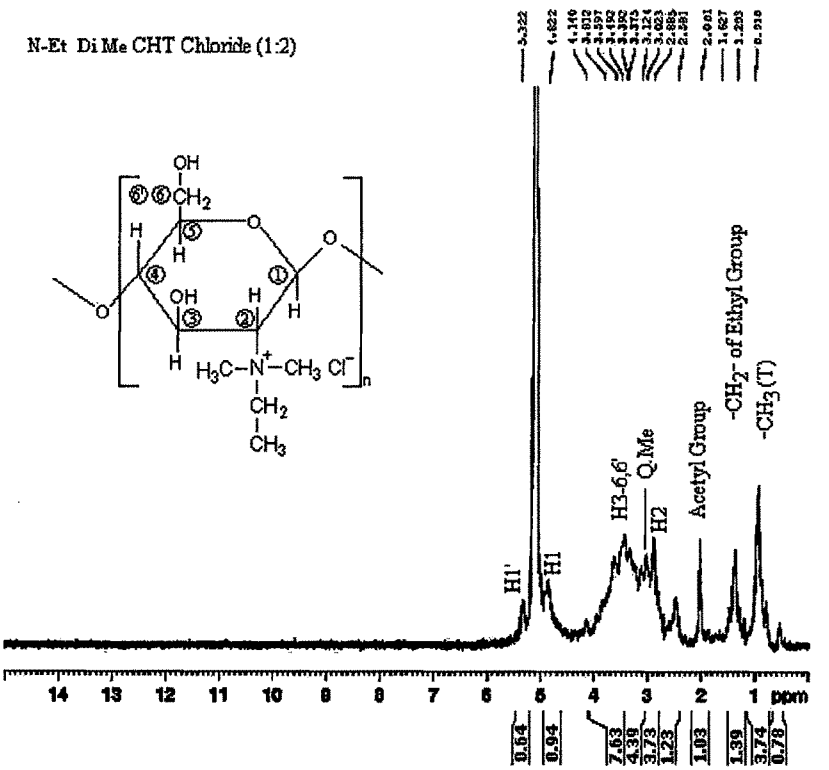



**Figure 4.10** [1]HNMR spectrum of *N*- ethyl *N*, *N*-dimethyl chitosan chloride (1:2)

Various peaks and their intensities depicted by [1]HNMR of N-QEtCHT (1:2) and the determined DQ are summarized below.

| | | |
|---|---|---|
| $I_{Me(T)}$=3.74 | $\delta_{Me(t)}$= 0.9201 | Three protons (3H) of terminal methyl of ethyl chain. |
| $I_{Et}$ = | $\delta_{(CH2)}$ = 1.293 | 2 protons (2H) of 1 methylene group of ethyl chain |
| $I_{(CH2)}$ = 1.39 | | |
| n = 5 | | 5 protons ethyl group [-$CH_2$-$CH_3$] |

| | | |
|---|---|---|
| $I_{NAc}$ = 1.0 | $\delta_{(NAc)}$ =2.001 | Three protons (3H) methyl terminal of acetyl group. -N-CO-$CH_3$ |
| $I_{H2}$ = 3.73 | $\delta_{(H2)}$ = 2.885 | One proton (1H) bound to C2 glucosamine (GlcN) residue. |
| $I_{H3\text{-}6,6'}$ = 7.63 | $\delta_{(H3\text{-}6,6')}$ = 3.2-4.5 | Five protons (5H) bounded to C-3,4,5,6 & 6' of GlcN. |
| $I_{QMe}$= 4.39 | $\delta_{(QMe)}$ =3.124 | Six protons (6H) of two methyl groups attached to N-ethyll substituted of GlcN residue. |
| $I_{DiMe}$= 1.23 | $\delta_{(DiMe)}$ =2.581 | Six protons (6H) of two methyl groups attached to free amino groups of GlcN residue. |
| $I_{H1}$ = 0.94 | $\delta_{(H1)}$ = 4.432 | One anomeric proton (1H) of the glucosamine units |
| $I_{H1'}$ = 0.64 | $\delta_{(H1)}$ = 5.422 | One anomeric proton (1H) of the N-acetyl glucosamine units |
| I= 0.18 | $\delta$ = 0.78 | |

**DS = 45.5 %**

From these data, the degree of quaternization (DQ, %) is calculated by using the equation 4.12 as follows.

$$DQ\,(\%) = \frac{I_{QMe}}{6\left[I_{H1} + I_{H1'}\right]} X100 \qquad \textbf{(4.12)}$$

$$= \frac{4.39}{6\left[0.94 + 0.64\right]} X100 = \textbf{46.3 \%}$$

The digit '6' at the denominator of right hand side is the number of protons of two methyl groups attached to ethyl substituted N of GlcN residue.

***N- Ethyl chitosan [N- Et CHT (1:4])***

Various peaks ($\delta$) with corresponding integrals (I) for N-Et CHT (1:4) (Figure not shown) and the determined DS values using the equations 4.10 and 4.11 are presented as follows:

| | | |
|---|---|---|
| $\delta_{Me(t)}$= 0.954ppm | $I_{Me(T)}$ = 4.67 | Three protons (3H) of terminal methyl of ethyl chain. |
| $\delta_{(CH2)}$ = 1.323 ppm | $I_{Et}$ = $I_{(CH2)}$ = 2.82 | 2 protons (2H) of one methylene group of ethyl chain |
| n = 5 | | 5 protons ethyl group [-$CH_2$-$CH_3$] |
| $\delta_{(NAc)}$ =1.947 ppm | $I_{NAc}$ = 1.07 | Three protons (3H) methyl terminal of acetyl group -N-CO-$CH_3$ |
| $\delta_{(H2)}$ = 2.854 ppm | $I_{H2}$ = 1.78 | One proton (1H) bound to C2 glucosamine (GlcN) residue. |
| $\delta_{(H3\text{-}6,6')}$ = 3.2-4.5 ppm | $I_{H3\text{-}6,6'}$ = 3.33+3.89 =2.22 | Five protons (5H) bounded to C-3,4,5,6 & 6' of GlcN. |
| $\delta_{(H1)}$ = 4.601 ppm | $I_{H1}$ = 1.00 | One anomeric proton (1H)of the glucosamine units |
| $\delta_{(H1)}$ = 5.174 ppm | $I_{H1'}$ = 0.69 | One anomeric proton (1H) of the N-acetyl glucosamine units |

DS = Method1: 83.47%, Method 2: 81.71%, Average DS = **82.6 %**

### *$^1$NMR Spectrum analysis of N- butyl chitosan [N- Bu CHT (1:2)]*

The $^1$HNMR spectrum of the *N*-Bu CHT (1:2) is shown in Figure 4.11.

Various peaks (δ) with corresponding integrals (I) for N-Bu CHT (1:2) depicted by $^1$HNMR spectrum and the DS (%) evaluated using equations 4.10 and 4.11 are presented below.

| | | |
|---|---|---|
| $\delta_{Me(t)}$= 0.968ppm | $I_{Me(T)}$ = 2.03 | Three protons (3H) of terminal methyl of butyl chain. |
| $\delta_{(CH2)}$ =1.376ppm | $I_{Bu}$ =$I_{(CH2)3}$- = 2.60 | 6 protons (6H) of three methylene group of butyl chain |
| n = 9 | | 9 protons butyl group [- $(CH_2)_3$-$CH_3$] |
| $\delta_{(NAc)}$ =2.081ppm | $I_{NAc}$ = 1.0 | Three protons (3H) methyl terminal of acetyl group. -N-CO-$CH_3$ |

| | | |
|---|---|---|
| $\delta_{(H2)}$ = 3.008ppm | $I_{H2}$ = 1.74 | One proton (1H) bound to C2 glucosamine (GlcN) residue. |
| $\delta_{(H3\text{-}6,6')}$ = 3.1-4.2 ppm | $I_{H3\text{-}6,6'}$ = 5.75 | Five protons (5H) bounded to C-3,4,5,6 & 6' of GlcN. |
| $\delta_{(H1)}$ = 4.588ppm | $I_{H1}$ = 0.63 | One anomeric proton (1H) of the glucosamine units |
| $\delta_{(H1')}$ = 5.533ppm | $I_{H1'}$ = 0.48 | One anomeric proton (1H) of the N-acetyl glucosamine units |

D.S. = 39.04, 41.21, Average **DS = 40.1 %**

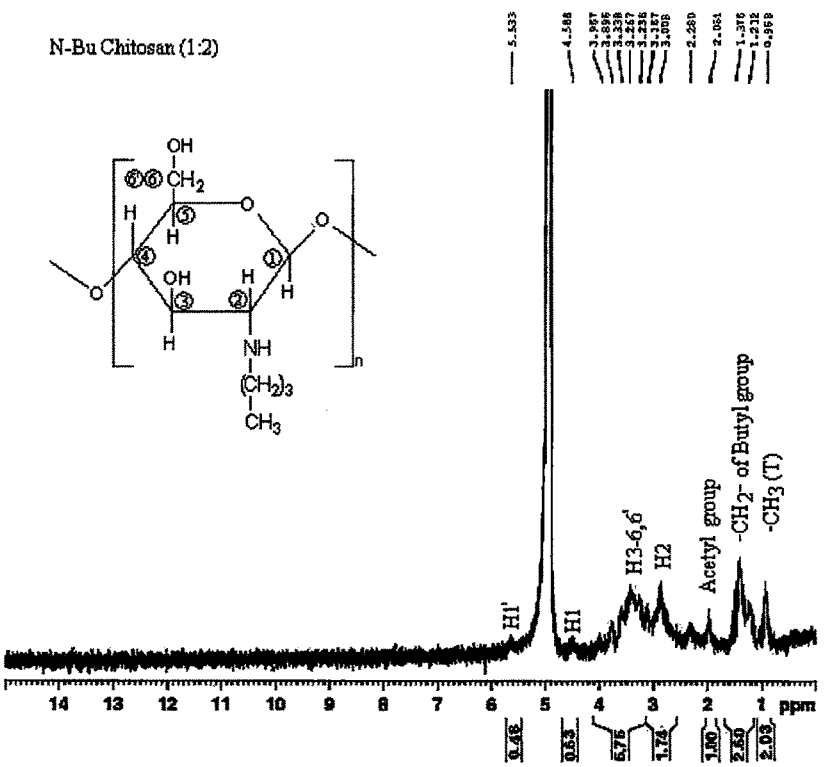



**Figure 4.11** $^1$HNMR spectrum of *N*-butyl chitosan (1:2)

***$^1$NMR Spectrum analysis of N- Butyl N, N-dimethyl chitosan chloride (1:2) [N-Bu Q CHT(1:2)]***

The H$^1$NMR spectrum of N Butyl N,N dimethyl chitosan chloride is shown in Figure 4.12.

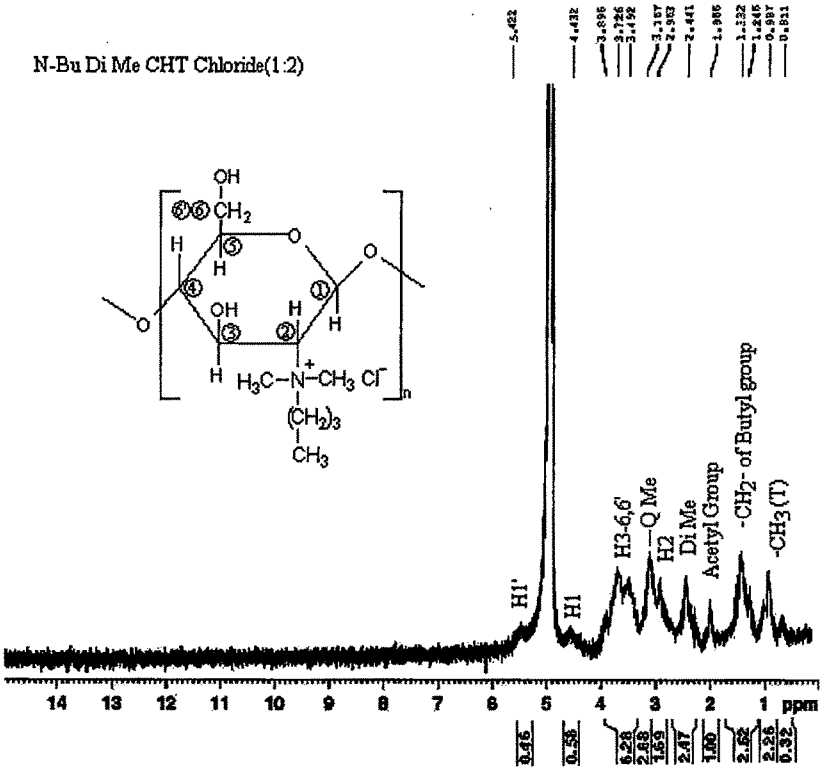



**Figure 4.12** $^{1}$HNMR spectrum of *N*-butyl *N, N*-dimethyl chitosan chloride (1:2)

Various peaks (δ) with corresponding integrals (I) for N-Bu Q CHT (1:2) depicted by $^{1}$HNMR spectrum and the DQ determined using equation 4.12 are summarized as below.

| | | |
|---|---|---|
| $\delta_{Me(t)}$= 0.987 ppm | $I_{Me(T)}$=2.26 | Three protons (3H) of terminal methyl of ethyl chain. |
| $\delta_{(CH2)3}$ = 1.332ppm | $I_{Bu}$ = $I_{(CH2)3}$ = 2.52 | 6 protons (6H) of three methylene group of butyl chain |
| n = 9 | | 9 protons butyl group [- $(CH_2)_3$-$CH_3$] |
| $\delta_{(NAc)}$=1.966 ppm | $I_{NAc}$ = 1.0 | Three protons (3H) methyl terminal of acetyl group -N-CO-$CH_3$ |
| $\delta_{(H2)}$ = 2.893 ppm | $I_{H2}$ = 1.69 | One proton (1H) bound to C2 glucosamine (GlcN) residue. |
| $\delta_{(H3\text{-}6,6')}$ = 3.2-4.2 ppm | $I_{H3\text{-}6,6'}$ = 6.28 | Five protons (5H) bounded to C-3,4,5,6 & 6' of GlcN. |

| | | |
|---|---|---|
| $\delta_{(QMe)}$=3.108 ppm | $I_{QMe}$= 2.68 | Six protons (6H) of two methyl groups attached to N- butyl substituted of GlcN residue. |
| $\delta_{(DiMe)}$=2.411 ppm | $I_{DiMe}$= 2.47 | Six protons (6H) of two methyl groups attached to free amino groups of GlcN residue. |
| $\delta_{(H1)}$= 4.432 ppm | $I_{H1}$ = 0.58 | One anomeric proton (1H) of the glucosamine units |
| $\delta_{(H1')}$= 5.422 ppm | $I_{H1'}$ = 0.46 | One anomeric proton (1H) of the N-acetyl glucosamine units |
| $\delta$ = 0.811 ppm | I= 0.32 | |
| **DS (%) =40.1 %** | | |
| **DQ (%) =42.9 %** | | |

***$^1$NMR spectrum analysis of N- butyl chitosan [N- Bu CHT (1:4)]***

Various peaks ($\delta$) with corresponding integrals (I) for N-BuCHT(1:4) depicted by $^1$HNMR spectrum (figure not shown) and the DS determined using equations 4.10 and 4.11 are summarized as below.

| | | |
|---|---|---|
| $\delta_{Me(t)}$= 0.921ppm | $I_{Me(T)}$ = 1.80 | Three protons (3H) of terminal methyl of ethyl chain. |
| $\delta_{(CH2)}$=1.476, 1.322 ppm | $I_{Bu}$ = $I_{(CH2)3}$ = 3.82 | 6 protons (6H) of three methylene group of butyl chain |
| | n = 9 | 9 protons butyl group,-$(CH_2)_3$-$CH_3$ |
| $\delta_{(NAc)}$=1.962 ppm | $I_{NAc}$ = 0.78 | Three protons (3H) methyl terminal of acetyl group, -N-CO-$CH_3$ |
| $\delta_{(H2)}$= 2.960 ppm | $I_{H2}$ = 1.67 | One proton (1H) bound to C2 glucosamine (GlcN) residue. |
| $\delta_{(H3\text{-}6,6')}$= 3.2-4.5 ppm | $I_{H3\text{-}6,6'}$ = 3.70 | Five protons (5H) bounded to C-3,4,5,6 & 6' of GlcN. |
| $\delta_{(H1)}$= 4.551 ppm | $I_{H1}$ = 0.52 | One anomeric proton (1H)of the glucosamine units |
| $\delta_{(H1)}$= 5.614 ppm | $I_{H1'}$ = 0.38 | One anomeric proton (1H) of the N-acetyl glucosamine units |

D.S. = 71.85 & 70.52% , Average **DS = 71.2 %**

***$^1$NMR spectrum analysis of N- dodecyl chitosan (1:2) [N- DodCHT(1:2)]***

Various peaks (δ) with corresponding integrals (I) for N-DodCHT (1:2) depicted by $^1$HNMR spectrum (figure not shown) and the DS determined using equations 4.10 and 4.11 are summarized as below.

| | | |
|---|---|---|
| $\delta_{Me(t)}$= 0.903ppm | $I_{Me(T)}$ = 1.52 | Three protons (3H) of terminal methyl of dodecyl chain. |
| $\delta_{(CH2)}$=1.376ppm | $I_{Dod}$ = $I_{(CH2)11}$=2.44 | 22 protons (22H) of 11 methylene groups of dodecyl chain |
| n = 25 | | 25 protons dodecyl group [- $(CH_2)_{11}$-$CH_3$] |
| $\delta_{(NAc)}$=2.011ppm | $I_{NAc}$ = 1.0 | Three protons (3H) methyl terminal of acetyl group. -N-CO-$CH_3$ |
| $\delta_{(H2)}$ = 3.061 ppm | $I_{H2}$ = 1.49 | One proton (1H) bound to C2 glucosamine (GlcN) residue. |
| $\delta_{(H3\text{-}6,6')}$ = 3.2-4.5 ppm | $I_{H3\text{-}6,6'}$ = 3.00 | Five protons (5H) bounded to C-3,4,5,6 & 6' of GlcN. |
| $\delta_{(H1)}$ = 4.638 ppm | $I_{H1}$ = 0.31 | One anomeric proton (1H)of the glucosamine units |
| $\delta_{(H1')}$ = 5.403 ppm | $I_{H1'}$ = 0.17 | One anomeric proton (1H) of the N-acetyl glucosamine units |

**DS = 23.11% & 21.16%, Average DS = 22.1 %**

***$^1$NMR spectrum analysis of N- dodecyl chitosan [N- DodCHT (1:4)]***

The $^1$HNMR spectrum of N- dodecyl chitosan is shown in Figure 4.13.

Various peaks (δ) with corresponding integrals (I) for N-DodCHT (1:4) depicted by $^1$HNMR spectrum and the DS determined using equations 4.10 and 4.11 are summarized as below.

| | | |
|---|---|---|
| $\delta_{Me(t)}$= 0.912ppm | $I_{Me(T)}$ = 2.56 | Three protons (3H) of terminal methyl of dodecyl chain. |

| | | |
|---|---|---|
| $\delta_{(CH2)}$=1.413ppm | $I_{Dod}$ = $I_{(CH2)11-}$ = 4.69 | 22 protons (22H) of three methylene group of dodecyl chain |
| n = 25 | | 25 protons dodecyl group,-($CH_2$)$_{11}$-$CH_3$ |
| $\delta_{(NAc)}$=2.000 ppm | $I_{NAc}$ = 1.0 | Three protons (3H) methyl terminal of acetyl group, -N-CO-$CH_3$ |
| $\delta_{(H2)}$ = 2.919 ppm | $I_{H2}$ = 1.68 | One proton (1H) bound to C2 glucosamine (GlcN) residue. |
| $\delta_{(H3\text{-}6,6')}$ = 3.1-4.2 ppm | $I_{H3\text{-}6,6'}$ = 3.00 | Five protons (5H) bounded to C-3,4,5,6 & 6' of GlcN. |
| $\delta_{(H1)}$ = 4.588 ppm | $I_{H1}$ = 0.35 | One anomeric proton (1H) of the glucosamine units |
| $\delta_{(H1)}$ = 5.533 ppm | $I_{H1'}$ = 0.21 | One anomeric proton (1H) of the N-acetyl glucosamine units |

DS (%)= 38.07, 37.18, Average **DS = 37.6 %**

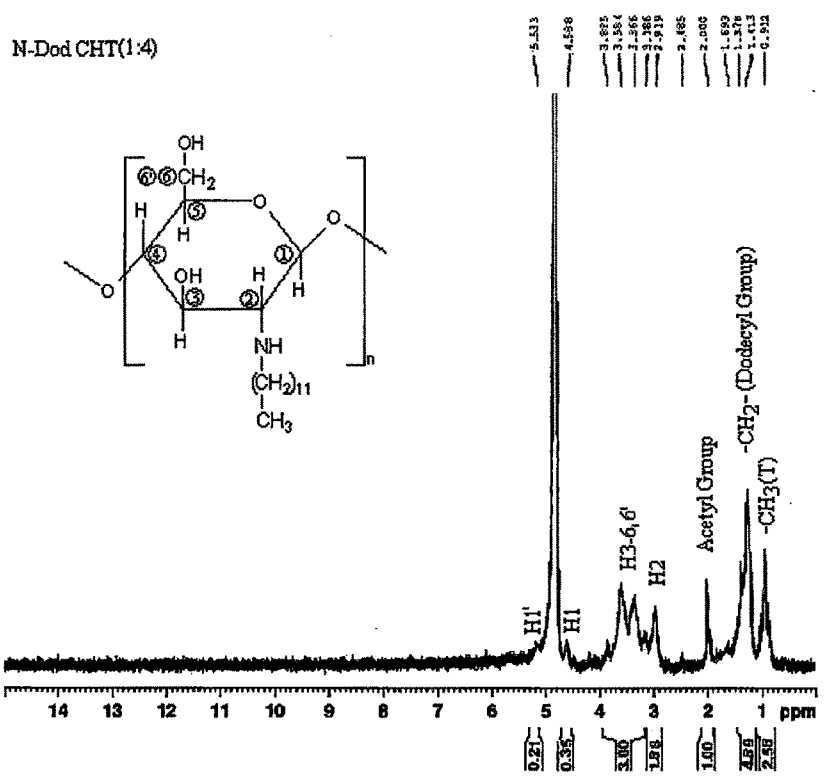



**Figure 4.13** $^1$HNMR spectrum of *N*- dodecyl chitosan (1:4)

***$^1$NMR spectrum analysis of N- dodecyl N, N-dimethyl chitosan chloride (1:4) [N-DodQCHT(1:4)]***

The $^1$HNMR spectrum of *N*- dodecyl N, N-dimethyl chitosan chloride (1:4) is shown in Figure 4.14.

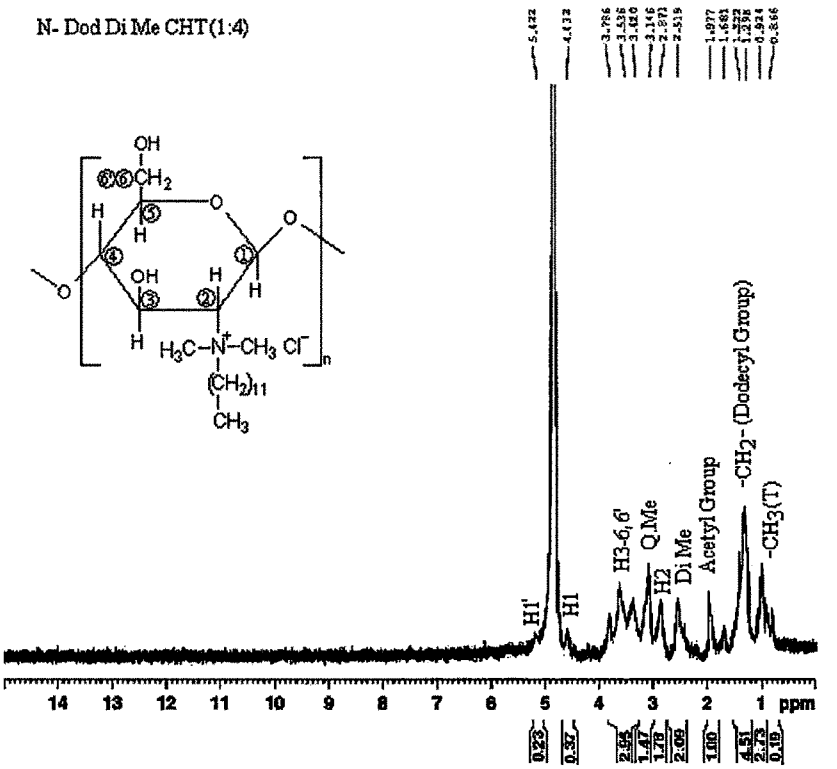



**Figure 4.14** $^1$HNMR spectrum of *N*- dodecyl *N*, *N*-dimethyl chitosan chloride (1:4)

Various peaks (δ) with corresponding integrals (I) for N-Dod Q CHT(1:4) depicted by $^1$HNMR and the DQ determined using equation 4.12 are summarized as below.

| | | |
|---|---|---|
| $\delta_{Me(t)}$= 0.924ppm | $I_{Me(T)}$=2.73 | Three protons (3H) of terminal methyl of dodecyl chain. |
| $\delta_{(CH2)}$=1.298ppm | $I_{Dod}$ = $I_{(CH2)11-}$ = 4.51 | 22 protons (22H) of three methylene group of dodecyl chain |
| n = 25 | | 25 protons dodecyl group,- $(CH_2)_{11}$-$CH_3$ |

| | | |
|---|---|---|
| $\delta_{(NAc)}$=1.977ppm | $I_{NAc}$ = 1.0 | Three protons (3H) methyl terminal of acetyl group. -N-CO-$CH_3$ |
| $\delta_{(H2)}$ = 2.871 ppm | $I_{H2}$ = 1.76 | One proton (1H) bound to C2 glucosamine (GlcN) residue. |
| $\delta_{(H3\text{-}6,6')}$ = 3.2-4.2 ppm | $I_{H3\text{-}6,6'}$ = 2.95 | Five protons (5H) bounded to C-3,4,5,6 & 6' of GlcN. |
| $\delta_{(QMe)}$=3.146ppm | $I_{QMe}$= 1.47 | Six protons (6H) of two methyl groups attached to *N*- dodecyl substituted of GlcN residue. |
| $\delta_{(DiMe)}$=2.519ppm | $I_{DiMe}$= 2.09 | Six protons (6H) of two methyl groups attached to free amino groups of GlcN residue. |
| $\delta_{(H1)}$ = 4.432 ppm | $I_{H1}$ = 0.37 | One anomeric proton (1H) of the glucosamine units. |
| $\delta_{(H1')}$ = 5.422 ppm | $I_{H1'}$ = 0.23 | One anomeric proton (1H) of the N-acetyl glucosamine units. |
| $\delta$ = 0.866 ppm | I= 0.19 | |

**DS (%) =37.6 %, DQ (%) =40.8 %**

#### *4.3.1.2.4 Elemental analysis*

The degree of substitution (DS) of *N*- substituted CHT was calculated from C/N value of elemental analysis using the formula 4.9 [18, 60].

$$\frac{C1}{N1}\times(1-DS)+\frac{C2}{N2}\times DS=\frac{C3}{N3}DAC \qquad \textbf{(4.9)}$$

Where, C1/N1 is calculated from the formula of non substituted CHT i.e. glucosamine residue (GlcN), C2/N2 from the N-Substituted residue and C3/N3 is found value of sample by elemental analysis. DAC is degree of deacetylation, 0.9 (i.e.90 %.).The percentage CHN content of selected chitosan derivatives determined by the elemental analysis is presented in Table 4.13 and the evaluated DS values of these derivatives in Table 4.19.

**Table 4.13** Elemental analysis (CHN) data of different *N*-sub CHT derivatives

| Sample | Theoretical values | | Elemental Analysis, | | | |
|---|---|---|---|---|---|---|
| | C1/N1 | C2/N2 | C, % | H , % | N, % | C3/N3 |
| CHT | 5.14 | 6.86 | 35.52 | 6.75 | 5.33 | 5.33 |
| TMCHT (1:10) | 5.14 | 7.71 | 40.19 | 7.04 | 6.26 | 6.26 |
| TMCHT (1:15) | 5.14 | 7.71 | 44.63 | 7.07 | 7.11 | 7.11 |
| N-Et CHT (1:2) | 5.14 | 6.86 | 40.84 | 7.24 | 6.62 | 6.62 |
| N-Bu CHT(1:2) | 5.14 | 8.57 | 44.97 | 7.84 | 7.36 | 7.36 |
| N-Dod CHT(1:4) | 5.14 | 15.43 | 59.06 | 8.33 | 10.20 | 10.20 |
| N-Bz CHT (1:4) | 5.14 | 11.14 | 50.58 | 7.53 | 8.53 | 8.53 |
| N-Np CHT(1:4) | 5.14 | 14.57 | 54.38 | 7.96 | 9.36 | 9.36 |

*C1/N1 is calculated from the formula of non substituted CHT i.e. glucosamine (GlcN) residue, C2/N2 from the formula of N-Substituted residue using the Table 4.12*

Calculations:

*Determination of DS of N-ethyl chitosan (1:2) [N-Et CHT (1:2)]*

The DS determined from the elemental (CHN) analysis data and using the expression 4.9 for N-Et CHT (1:2) can be illustrated as follows.

$$\frac{C1}{N1}\times(1-DS)+\frac{C2}{N2}\times DS=\frac{C3}{N3}DAC \qquad \textbf{(4.9)}$$

$$\frac{C1}{N1}\times(1-DS)+\frac{C2}{N2}\times DS=\frac{C3}{N3}\times 0.9$$

$$5.14\times(1-DS)+6.86\times DS=6.62\times 0.9$$

$\therefore$ DS = 0.4756 ethyl groups per glucosamine unit OR 47.6 %

Similarly, the DS of *N*-butyl chitosan (1:2)[N-BuCHT (1:2)] and *N*-dodecyl chitosan (1:4)[N-DodCHT (1:4)] was found to be 43.27 % and 39.26 % respectively

### *4.3.1.2.5 Conductometric titrations*

Degree of quaternization of quaternized *N*-alkyl chitosan chloride derivatives were also determined conductometrically by the titration against 0.1M $AgNO_3$ and using the expression 4.1 as discussed earlier in section 4.3.1.1.3.

**Table 4.14** Conductometric titrations readings for *N*-alkyl Q CHT derivatives

| $AgNO_3$ (0.1M) | Conductance (mMhos) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | N-Et Q CHT (1:2) | | | N-Et Q CHT (1:4) | | | N-Bu Q CHT (1:2) | | | N-Bu Q CHT (1:4) | | |
| | I | II | III | I | II | III | I | II | III | I | II | III |
| 0 | 3.30 | 3.30 | 3.40 | 3.70 | 3.75 | 3.70 | 4.00 | 4.00 | 4.00 | 4.10 | 4.10 | 4.00 |
| 0.5 | 3.25 | 3.20 | 3.25 | 3.65 | 3.70 | 3.70 | 3.75 | 3.80 | 3.90 | 4.00 | 4.00 | 3.90 |
| 1.0 | 3.15 | 3.10 | 3.20 | 3.50 | 3.50 | 3.55 | 3.65 | 3.75 | 3.75 | 3.75 | 3.80 | 3.80 |
| 1.5 | 2.95 | 3.00 | 3.00 | 3.30 | 3.40 | 3.40 | 3.50 | 3.60 | 3.65 | 3.55 | 3.60 | 3.75 |
| 2.0 | 2.80 | 2.85 | 2.80 | 3.20 | 3.30 | 3.35 | 3.30 | 3.40 | 3.35 | 3.35 | 3.35 | 3.35 |
| 2.5 | 2.70 | 2.75 | 2.65 | 3.05 | 3.25 | 3.25 | 3.15 | 3.25 | 3.25 | 3.20 | 3.25 | 3.30 |
| 3.0 | 2.50 | 2.60 | 2.60 | 2.95 | 3.00 | 2.95 | 3.00 | 3.15 | 3.10 | 3.00 | 3.00 | 3.15 |
| 3.5 | 2.45 | 2.50 | 2.50 | 2.85 | 2.90 | 2.90 | 2.95 | 3.10 | 3.10 | 2.75 | 2.80 | 2.80 |
| 4.0 | 2.35 | 2.30 | 2.35 | 2.60 | 2.70 | 2.75 | 2.60 | 2.75 | 2.65 | 2.65 | 2.75 | 2.70 |
| 4.5 | 2.15 | 2.20 | 2.25 | 2.40 | 2.60 | 2.60 | 2.50 | 2.70 | 2.60 | 2.50 | 2.50 | 2.60 |
| 5.0 | 2.18 | 2.15 | 2.15 | 2.30 | 2.50 | 2.35 | 2.30 | 2.50 | 2.55 | 2.25 | 2.30 | 2.30 |
| 5.5 | 2.00 | 2.05 | 2.10 | 2.25 | 2.35 | 2.30 | 2.25 | 2.40 | 2.35 | 2.00 | 2.10 | 2.15 |
| 6.0 | 1.80 | 1.85 | 1.85 | 2.15 | 2.20 | 2.15 | 2.00 | 2.05 | 2.10 | 1.90 | 2.00 | 2.10 |
| 6.5 | 1.75 | 1.80 | 1.85 | 1.95 | 2.00 | 2.00 | 1.75 | 1.80 | 1.90 | 1.75 | 1.75 | 1.75 |
| 7.0 | 1.60 | 1.65 | 1.60 | 1.85 | 1.90 | 1.90 | 1.60 | 1.65 | 1.75 | 1.70 | 1.70 | 1.70 |
| 7.5 | 1.5 | 1.6 | 1.5 | 1.75 | 1.80 | 1.85 | 1.50 | 1.50 | 1.55 | 1.75 | 1.75 | 1.75 |
| 8.0 | 1.35 | 1.40 | 1.40 | 1.55 | 1.70 | 1.65 | 1.60 | 1.60 | 1.50 | 2.00 | 2.00 | 2.05 |
| 8.5 | 1.25 | 1.30 | 1.35 | 1.50 | 1.55 | 1.60 | 1.35 | 1.35 | 1.35 | - | - | - |
| 9.0 | 1.20 | 1.25 | 1.25 | 1.40 | 1.50 | 1.50 | 1.75 | 1.75 | 1.80 | 2.90 | 2.95 | 2.95 |
| 9.5 | 1.10 | 1.15 | 1.15 | 1.35 | 1.40 | 1.45 | - | - | - | - | - | |
| 10.0 | 1.00 | 1.05 | 1.05 | 1.25 | 1.30 | 1.35 | 2.20 | 2.25 | 2.20 | 3.75 | 3.70 | 3.70 |
| 10.5 | 1.25 | 1.25 | 1.25 | 1.35 | 1.35 | 1.40 | - | - | - | - | - | - |
| 11.0 | 2.00 | 1.95 | 2.00 | 2.00 | 2.00 | 2.05 | 3.60 | 3.60 | 3.65 | 4.50 | 4.60 | 4.55 |
| 12.0 | 3.50 | 3.40 | 3.50 | 3.25 | 3.00 | 3.30 | 4.50 | 4.40 | 4.50 | 5.40 | 5.50 | 5.50 |
| 13.0 | 4.90 | 5.00 | 4.90 | 4.50 | 4.60 | 4.60 | 5.40 | 5.50 | 5.40 | 6.25 | 6.25 | 6.30 |
| 14.0 | 6.25 | 6.30 | 6.30 | 6.00 | 5.90 | 6.05 | 6.25 | 6.25 | 6.30 | 7.00 | 7.05 | 7.10 |
| 15.0 | 7.90 | 7.80 | 7.75 | 7.25 | 7.30 | 7.25 | 7.20 | 7.25 | 7.25 | 7.90 | 8.00 | 7.90 |

*NMP=40ml, CHT:$CH_3I$=1:15, CHT: NaOH =1:2*

**Table 4.15** Conductometric titrations readings for *N*-alkyl Q CHT derivatives

| $AgNO_3$ (0.1M) | Conductance (mMhos) | | | | | |
|---|---|---|---|---|---|---|
| | N-Dod Q CHT (1:2) | | | N-Dod Q CHT (1:4) | | |
| | I | II | III | I | II | III |
| 0 | 3.70 | 3.65 | 3.75 | 3.80 | 3.75 | 3.80 |
| 0.5 | 3.50 | 3.45 | 3.60 | 3.65 | 3.60 | 3.70 |
| 1.0 | 3.40 | 3.30 | 3.50 | 3.50 | 3.65 | 3.60 |
| 1.5 | 3.15 | 3.10 | 3.15 | 3.30 | 3.25 | 3.35 |
| 2.0 | 3.00 | 2.90 | 3.00 | 3.25 | 3.20 | 3.30 |
| 2.5 | 2.75 | 2.70 | 2.80 | 3.00 | 3.00 | 3.00 |
| 3.0 | 2.60 | 2.55 | 2.70 | 2.85 | 2.85 | 2.90 |
| 3.5 | 2.40 | 2.45 | 2.55 | 2.75 | 2.65 | 2.70 |
| 4.0 | 2.25 | 2.25 | 2.30 | 2.55 | 2.50 | 2.60 |
| 4.5 | 2.15 | 2.20 | 2.20 | 2.40 | 2.45 | 2.50 |
| 5.0 | 2.15 | 2.15 | 2.20 | 2.35 | 2.35 | 2.35 |
| 5.5 | 2.25 | 2.25 | 2.25 | 2.20 | 2.25 | 2.25 |
| 6.0 | 2.60 | 2.60 | 2.60 | 2.25 | 2.20 | 2.25 |
| 6.5 | - | - | - | 2.50 | 2.50 | 2.50 |
| 7.0 | 3.25 | 3.20 | 3.25 | 3.60 | 3.60 | 3.65 |
| 8.0 | 3.90 | 3.85 | 3.80 | 4.25 | 4.30 | 4.30 |
| 9.0 | 4.50 | 4.50 | 4.50 | 5.00 | 5.00 | 5.00 |
| 10.0 | 5.00 | 5.00 | 5.10 | 5.75 | 5.80 | 5.80 |
| 11.0 | 5.65 | 5.70 | 5.70 | 6.50 | 6.55 | 6.50 |
| 12.0 | 6.25 | 6.25 | 6.30 | 7.25 | 7.25 | 7.25 |
| 13.0 | 6.90 | 6.85 | 6.90 | 8.00 | 7.90 | 8.00 |
| 14.0 | 7.40 | 7.50 | 7.50 | 8.60 | 8.60 | 8.65 |

*NMP=40ml, CHT:$CH_3I$=1:15, CHT: NaOH =1:2*

The calculation part is discussed below.

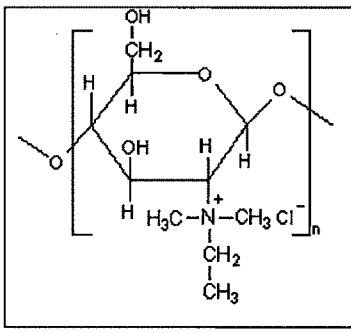
$$DQ\ (\%) = \frac{M_Q \times V \times [AgNO_3]}{m} X100 \qquad \textbf{(4.1)}$$

Where,

$M_Q$ is the molecular weight (g/mol) of repeating unit of the sample containing quaternized site, these values were obtained from the respective structural formula of derivatives given in Table 4.12. V and [$AgNO_3$] are the equivalent volume and concentration of $AgNO_3$ aqueous solution (0.1M) respectively and *m* (g) is the mass of

the sample which was 0.5g. The conductometric titration readings for *N*-alkyl Q CHT derivatives are presented in Table 4.14 and Table 4.15 and the calculated DQ values in Table 4.16 and Table 4.19.

*DQ of N-ethyl N, N- dimethyl chitosan (1:2) chloride[N-Et Q CHT(1:2)]*



| | |
|---|---|
| C,10 X 12 = | 120 |
| O, 4 X 16 = | 64 |
| H, 20 X 1 = | 20 |
| N,1 X 14 = | 14 |
| Cl,1X 35.5 = | 35.5 |
| $M_Q$ = | 253.5 |

$M_Q$= 253.5, m= 0.5 g, V = 10.2, 10.2, 10.4 = 10.27 ml **or** V= 0.01027 L

$$DQ\ (\%) = \frac{M_Q \times V \times [AgNO_3]}{m} X100$$

$$DQ\ (\%) = \frac{253.5 \times 0.01027 \times 0.1}{0.5} X100 = \mathbf{52.0\ \%}$$

*DQ of N-ethyl N,N-dimethyl chitosan (1:4) chloride[N-Et Q CHT(1:4)]*

$M_Q$= 253.5, m= 0.5 g, V= 10.3, 10.2, 10.4 = 10.3 ml or V= 0.0103 L

$$DQ\ (\%) = \frac{M_Q \times V \times [AgNO_3]}{m} X100$$

$$DQ\ (\%) = \frac{253.5 \times 0.0103 \times 0.1}{0.5} X100 = \mathbf{52.2\ \%}$$

Similarly, the DQ of other derivatives determined are presented in Table 4.16

**Table 4.16** Volume of 0.1M $AgNO_3$ required for lowest conductance value for different *N*-Alkyl Q CHT derivatives

| Sample | 0.1 M $AgNO_3$ titrant (V), ml | | | | DQ, % |
|---|---|---|---|---|---|
| | I | II | III | Average | |
| N-Et Q CHT (1:2) | 10.2 | 10.2 | 10.4 | 10.27 | 52.0 |
| N-Et Q CHT (1:4) | 10.3 | 10.2 | 10.4 | 10.30 | 52.2 |
| N-Bu Q CHT (1:2) | 8.4 | 8.4 | 8.5 | 8.43 | 47.5 |
| N-Bu Q CHT (1:4) | 7.3 | 7.3 | 7.2 | 7.27 | 40.9 |
| N-Dod Q CHT (1:2) | 5.9 | 5.8 | 6.0 | 5.90 | 46.4 |
| N-Dod Q CHT (1:4) | 5.7 | 5.8 | 5.7 | 5.73 | 45.1 |

*NMP=40ml, CHT:$CH_3I$=1:15, CHT: NaOH =1:2*

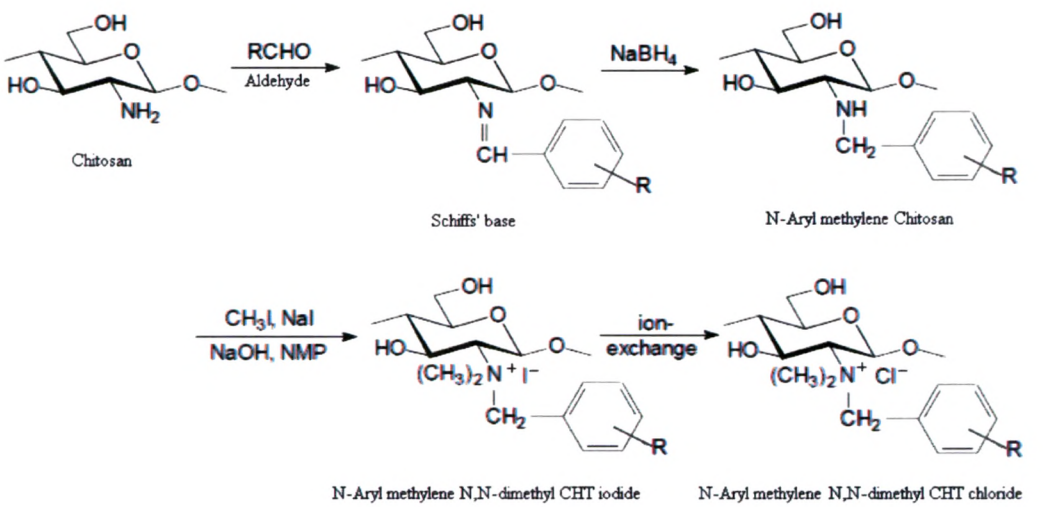
### *4.3.1.3 Synthesis of N-aryl N, N-dimethyl chitosan chloride*

Analogous to aliphatic aldehyde, different aromatic aldehydes namely benzaldehyde and 1-naphthyl aldehyde were employed in the Bosch reduction methodology in this project. Same two step protocol i.e. first, the reaction of CHT with aromatic aldehyde in acidic medium to form Schiff's base followed by the second step of reduction of Schiff's base to form secondary amine was followed. These *N*-substituted CHT derivatives were then subjected to quaternization by reaction with methyl iodide (fifteen fold excess) as discussed previously. Possibility of external control on the degree of substitution was studied by varying the mole proportions of the aldehyde by two fold excess and four fold excess with respect to the amine of chitosan. Concentrations of various reaction ingredients i.e. aromatic aldehydes and sodium borohydride ($NaBH_4$) are mentioned in Table 4.11 and the nomenclature of synthesized *N*-aryl CHT and quaternized *N*- aryl CHT in Table 4.12.

#### *4.3.1.3.1 Reaction mechanism*

The reaction mechanism is similar to that of aliphatic aldehyde. In brief, the primary amines of CHT readily add to the carbonyl group (>C=O) of aldehydes to form α- hydroxy amines, also called carbinolamines. These species undergo spontaneous elimination of water molecule to yield imines or Schiff's base [22]. This is also an electrophilic substitution reaction and follows $S_N2$ mechanism. The carbon-oxygen bond in carbonyl group of aldehydes is highly polarized due to the presence of electro-ve

oxygen. The electrons constituting the π bonds are partially shifted towards oxygen as a result of electromeric effect. It implies that the carbon atom of carbonyl group is electron deficient i.e. electrophile and therefore readily attacks nucleophilic amino group of CHT. The reaction schemes for the syntheses of *N*-benzyl *N,N* dimethyl chitosan chloride (N-Bz QCHT) and *N*-(1-naphthyl) methylene chitosan chloride (N-Np Q CHT) are illustrated in scheme 4.12.




**Scheme 4.12** Synthesis *N*-aryl *N,N*-dimethyl chitosan chloride

### *4.3.1.3.2 FTIR analysis of N-aryl CHT derivatives*

The FTIR spectra of *N*-benzyl and *N*-(1-Naphthyl) methylene chitosan and their corresponding quaternized derivatives are shown in Figure 4.15 and Figure 4.16 respectively. A strong absorption peak at around wave number 3081 cm-1 is assigned to C-H stretching of aromatic group and the band at 1456 cm-1 is one of the typical bands for C=C ring stretching of benzene. The aliphatic C-H stretch at about 2931 cm-1 is assigned to methylene group. In addition to aromatic C-H stretch and C=C ring stretch, a compound can be considered aromatic only if the spectrum has at least one strong absorption below 900 $cm^{-1}$ due to C-H bend out of benzene plane (-C=C-H bend) which are positioned at 896, 744 and 698 $cm^{-1}$ in Figure 4.15 [66]. The increase in intensity in absorption peak at 1451 $cm^{-1}$ in arylated quaternized chitosan in N-Bz Di Me CHT spectrum characterizes the attachment of methyl group.

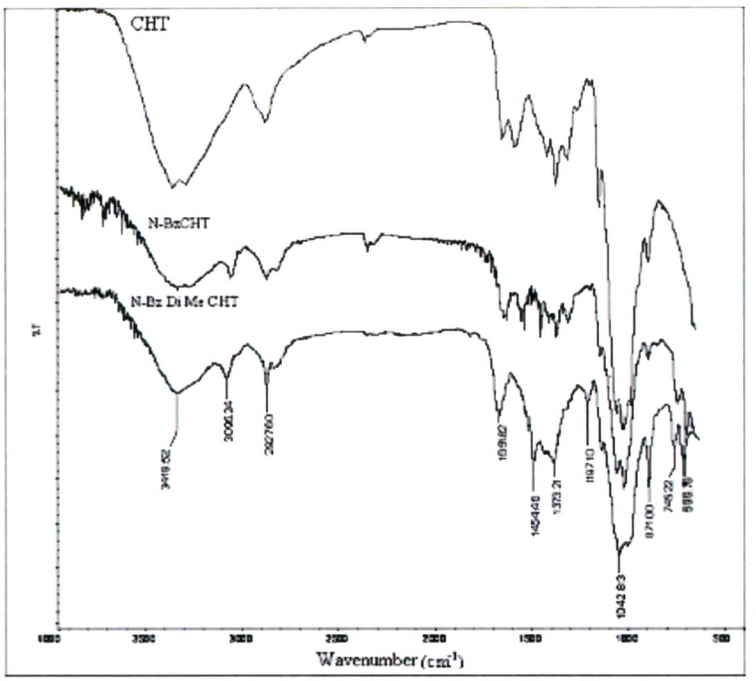



**Figure 4.15** FTIR spectra of *N*-benzyl *N,N*-dimethyl chitosan chloride

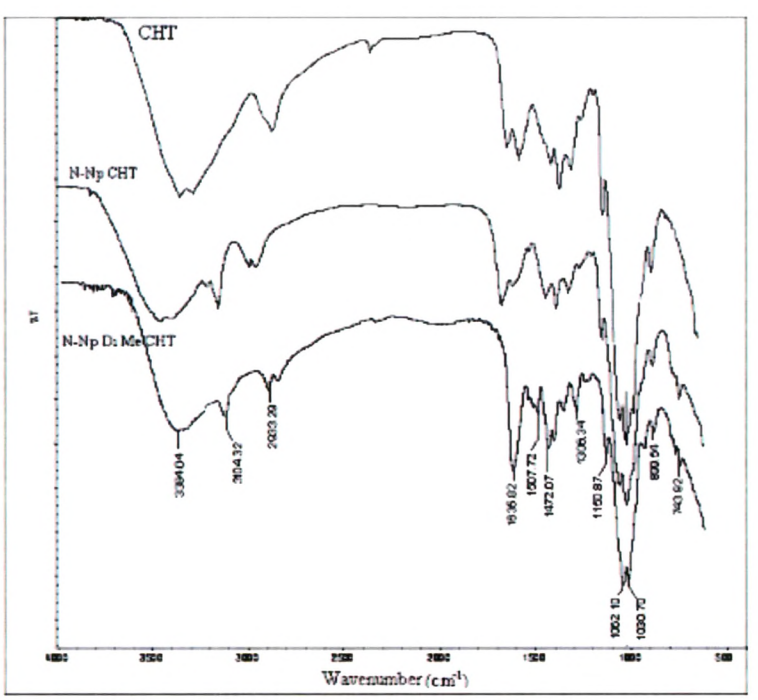



**Figure 4.16** FTIR spectra of *N*-(1-naphthyl) methylene *N,N*- dimethyl chitosan chloride derivative

Similar patterns are observed in *N*-(1-Naphthyl) methylene chitosan, Figure 4.16. These spectra of aryl substituted chitosan derivatives characterize successful attachment of benzyl and 1-naphthyl methylene groups and the also the methyl groups at nitrogen atom of CHT amine.

#### *4.3.1.3.3 $^1$HNMR spectroscopy*

In the $^1$HNMR spectrum, the aromatic proton resonances appear in the downfield region, mostly in $\delta$ =6 to 7 ppm, compared to the residual sugar protons and therefore they can be integrated with minimal interference leading to greater accuracy. Comparing the integrals due to aromatic protons with that of proton bonded to C2 or protons bonded to the sum of C2 and C3-6, 6'; one can evaluate the degree of substitution using the equations 4.11 and 4.13. The degree of substitution and degree of quaternization of these N-Aryl CHT determined from $^1$HNMR spectroscopy are presented in Table 4.19. The interpretations $^1$HNMR spectra of N- Bz CHT and N-Np CHT and their quaternized derivatives are discussed below.

#### *$^1$NMR Spectrum analysis of N- benzyl chitosan (1:4) [N- Bz CHT (1:4)]*

The $^1$HNMR spectrum of the *N*-benzyl Chitosan is shown in Figure 4.17.

The detailed analysis may be summarized as follows:

| | | |
|---|---|---|
| $\delta_{Ar}$= 6.693 ppm | $I_{Ar}$ = 2.41 | Five protons (**5H**) of aromatic group. |
| n = 5 | | Aromatic protons. |
| $\delta_{(NAc)}$ =1.983 ppm | $I_{NAc}$ = 1.0 | Three protons (3H) methyl terminal of acetyl group, -N-CO-C**H**$_3$ |
| $\delta_{(H2)}$ = 2.952 ppm | $I_{H2}$ = 1.05 | One proton (1H) bound to C2 glucosamine (GlcN) residue. |
| $\delta_{(H3\text{-}6,6')}$ = 3.2-4.5 ppm | $I_{H3\text{-}6,6'}$ = 5.54 | Five protons (5H) bounded to C-3,4,5,6 & 6' of GlcN. |
| $\delta_{(H1)}$ = 4.692 ppm | $I_{H1}$ = 0.53 | One anomeric proton (1H)of the glucosamine units |

$\delta_{(H1)}$ = 5.342 ppm  $I_{H1'}$ = 0.34  One anomeric proton (1H) of the N-acetyl glucosamine units

DS (%) = 45.90 & 43.88, **Average DS = 45 %**

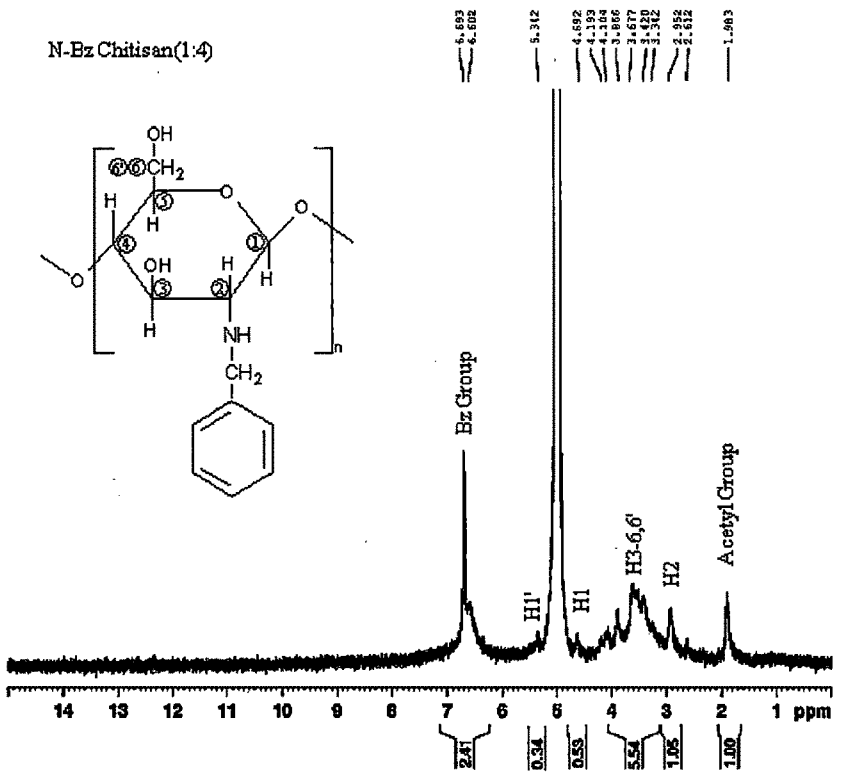



**Figure 4.17** $H^1$NMR spectrum of N-Benzyl chitosan (1:4)

Calculations:

The degree of substitution can be determined using the equation 4.11 as follows:

$$\frac{A}{[B+C]} = \frac{nDS}{6} \quad \textbf{OR} \quad \frac{I_{Ar}}{[I_{H2}+I_{H3-6}]} = \frac{nDS}{6} \qquad \textbf{(4.11)}$$

The digit '6' at the denominator of right hand side is the total number of protons at C2 of GlcN and C3,4,5,6 & 6'.

Where, DS is the degree substitution per GLcN residue.

A = Peak area of substituent, A= $I_{Ar}$ i.e. A= $I_{Ar}$ = 2.41

B = Peak area of H2 (proton at C2) of glucosamine residue (GlcN).

i.e. B = $I_{H2}$ = 1.05 at $\delta_{(H2)}$ = 2.952ppm for proton at C2 of GlcN.

C = Peak area of protons bounded to C-3,4,5,6 & 6' of GlcN.

C = $I_{H3\text{-}6,6'}$ = 5.54 (at δ= 3.2 to 4.5)

n= Number of proton per substituent = 5

Substituting these values in equation 4.11,

$$\frac{5\times DS}{6} = \frac{2.41}{[1.05+5.54]} = \frac{2.41}{6.59}$$

DS (%) = **43.9 %**

In another method, the degree of substitution can be calculated using the equation 4.13,

$$\frac{\textit{Signal Intensity due to H2}}{\textit{Signal Intensity due to aromatic protons}} = \frac{\textit{No of C2 protons per GlcN residue}}{\textit{No of aromatic protons per GlcN residue}}$$

$$\frac{I_{H2}}{I_{Ar}} = \frac{\textit{No of C2 protons per GlcN residue}}{\textit{No of aromatic protons per GlcN residue}} \qquad \textbf{(4.13)}$$

Number of protons bonded to C2 of GlcN residue is 1.

Let DS is the degree of substitution in % and 'n' is the number of protons bound to aromatic carbons.

Therefore, no of aromatic protons/ GlcN residue = $\frac{n\times DS}{100} = \frac{5\times DS}{100}$

$$\frac{I_{H2}}{I_{Ar}} = \frac{1}{\frac{5\times DS}{100}} \text{ OR } \frac{1\times 100}{5\times DS}$$

$$\text{DS} = \frac{1\times I_{Ar}\times 100}{5\times I_{H2}} = \frac{2.41\times 100}{5\times 1.05} = \textbf{45.9 \%}$$

**Average DS = 45 %**

***$^1$NMR Spectrum Analysis of N- benzyl N, N dimethyl chitosan chloride (1:4) [N-Bz Q CHT(1:4)]***

The $^1$HNMR spectrum of the *N*-benzyl *N,N* dimethyl chitosan chloride (1:4) is shown in Figure 4.18. In $^1$HNMR spectrum, the signal $\delta_{Ar}$= 6.602 ppm having the integral $I_{Ar}$ = 2.24 is assigned to benzyl group. The signals due to protons of quaternary methyl groups (two methyl groups attached to benzyl substituted N of GlcN residue) was found at $\delta_{QMe}$ = 3.261ppm with the intensity $I_{QMe}$ = 1.63.Methylation on unsubstituted amino groups was also traced at $\delta_{(DiMe)}$ =2.512 with the integral $I_{DiMe}$= 1.71. Other important signals recognized were: $\delta_{NAc}$ =1.961 ppm with integral $I_{NAc}$ = 1.0 for acetyl group, $\delta_{H2}$ = 2.897 ppm; $I_{H2}$ = 1.01 for proton bonded to C2 of GlcN residue, $\delta_{H3\text{-}6,6'}$ = 3.3-4.5 ppm; $I_{H3\text{-}6,6'}$ = 4.61 and the anomeric protons at $\delta_{(H1)}$ = 4.695 ppm; $I_{H1}$ = 0.47 and $\delta_{(H1)}$ = 5.304 ppm; $I_{H1'}$ = 0.33.The average DS determined earlier for the sample before quaternization was 43.88 % and the DQ % calculated from the equation 4.12 was 33.96 %.

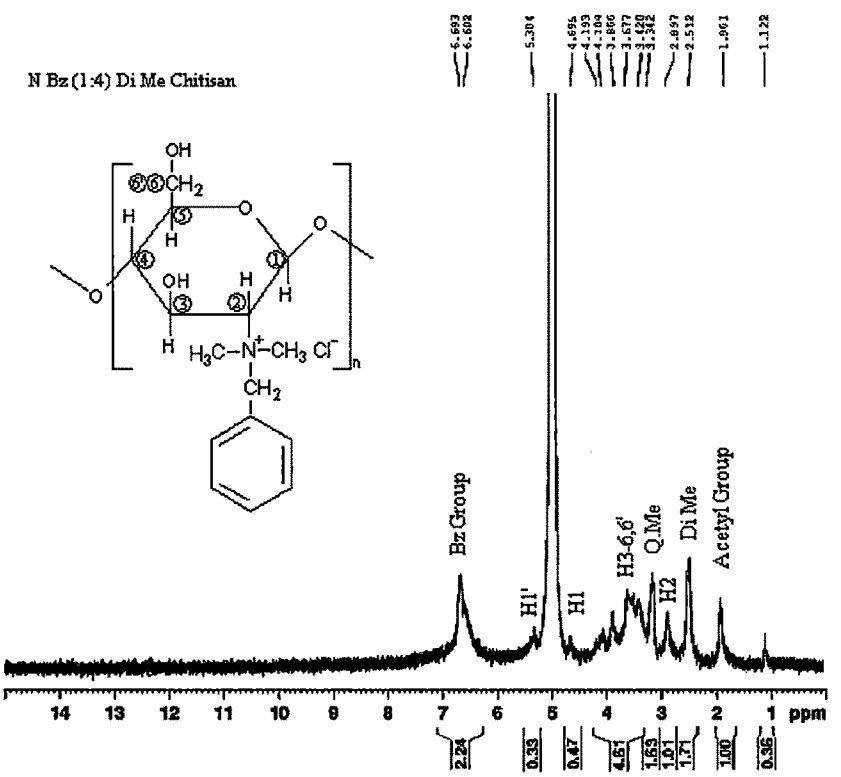



**Figure 4.18** $^1$HNMR spectrum of *N*- benzyl *N*, *N*- dimethyl chitosan chloride(1:4)

Calculations:

The degree of quaternization (DQ %) can be calculated using the equation 4.12 illustrated as follows.

$$DQ = \frac{I_{QMe}}{6[I_{H1} + I_{H1'}]} X100$$

$$= \frac{1.63}{6[0.47 + 0.33]} X100$$

$$= \mathbf{34\ \%}$$

***$^1$NMR Spectrum analysis of N- Benzyl chitosan (1:2) [N- Bz CHT (1:2)]***

Various peaks (δ) with corresponding integrals (I) for N-Bz CHT (1:4) depicted by $^1$HNMR spectrum (figure not shown) and the DS determined using expressions 4.11 and 4.13 are summarized below.

| | | |
|---|---|---|
| $\delta_{Ar}$= 6.7003ppm | $I_{Ar}$ = 1.04 | Five protons (**5H**) of aromatic group. |
| n = 5 | | Aromatic protons. |
| $\delta_{(NAc)}$ =1.986 ppm | $I_{NAc}$ = 1.0 | Three protons (3H) methyl terminal of acetyl group, -N-CO-**$CH_3$** |
| $\delta_{(H2)}$ = 3.001 ppm | $I_{H2}$ = 1.18 | One proton (1H) bound to C2 glucosamine (GlcN) residue. |
| $\delta_{(H3\text{-}6,6')}$ = 3.2-4.5 ppm | $I_{H3\text{-}6,6'}$ = 6.00 | Five protons (5H) bounded to C-3,4,5,6 & 6' of GlcN. |
| $\delta_{(H1)}$ = 4.694 ppm | $I_{H1}$ = 0.52 | One anomeric proton(1H) of the glucosamine units |
| $\delta_{(H1')}$ = 5.341 ppm | $I_{H1'}$ = 0.38 | One anomeric proton(1H) of the N-acetyl glucosamine units |

DS= 17.63 % & 17.39 %, Average **DS =17.5 %**

***$^1$NMR Spectrum analysis of N-(1-naphthyl) methylene chitosan (1:4) [N- NpCHT (1:4)]***

The $^1$HNMR spectrum of the *N*-(1-naphthyl) methylene chitosan (1:4) [N-NpCHT (1:4) is shown Figure 4.19.

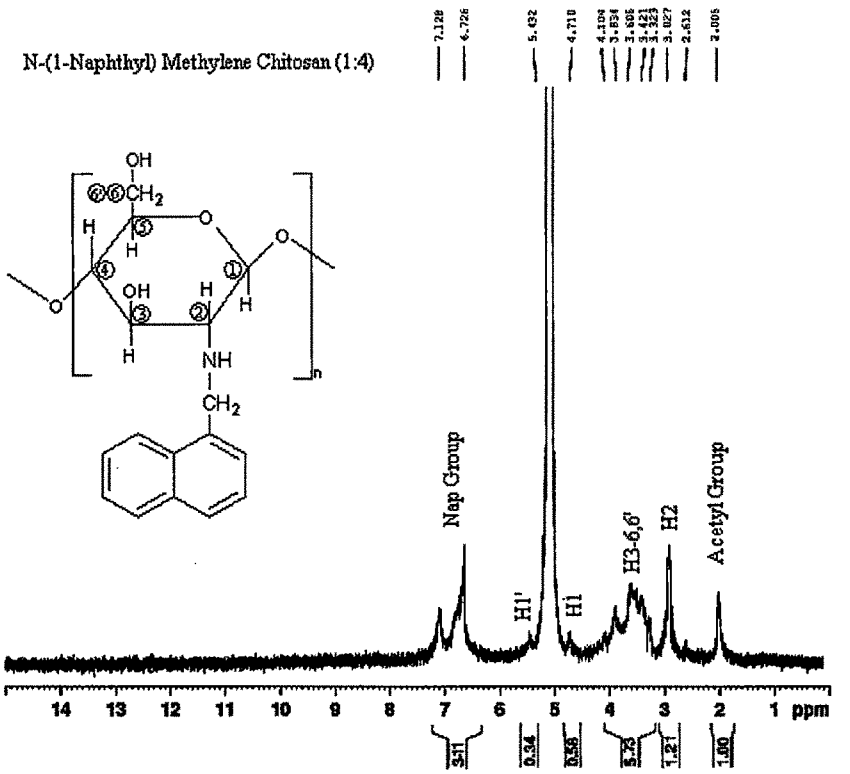



**Figure 4.19** $H^1$NMR spectrum of *N*-(1- naphthyl) methylene chitosan (1:4)

Various peaks (δ) with corresponding integrals (I) for N-Bz CHT (1:4) depicted by $^1$HNMR spectrum and the DS determined using equations 4.11 and 4.13 are summarized as below.

| | | |
|---|---|---|
| $\delta_{Ar}$= 6.726ppm | $I_{Ar}$ = 3.11 | Seven protons (**7H**) of aromatic group. |
| n = 7 | | Aromatic protons. |
| $\delta_{(NAc)}$=2.006 ppm | $I_{NAc}$ = 1.0 | Three protons (3H) methyl terminal of acetyl group, -N-CO-C**H**$_3$ |
| $\delta_{(H2)}$ = 3.027 ppm | $I_{H2}$ = 1.21 | One proton (1H) bound to C2 glucosamine (GlcN) residue. |
| $\delta_{(H3\text{-}6,6')}$ = 3.2-4.5 ppm | $I_{H3\text{-}6,6'}$ = 5.73 | Five protons (5H) bounded to C-3,4,5,6 & 6' of GlcN. |
| $\delta_{(H1)}$ = 4.710 ppm | $I_{H1}$ = 0.58 | One anomeric proton (1H)of the glucosamine units |

$\delta_{(H1')}$ = 5.432 ppm  $I_{H1'}$ = 0.47  One anomeric proton (1H) of the N-acetyl glucosamine units

DS= 36.72 & 38.41, Average **DS = 37.6 %**

***$^1$NMR spectrum analysis of N-(1- naphthyl) methylene N, N-dimethyl chitosan chloride (1:4) [N-Np Q CHT(1:4)]***

The $^1$HNMR spectrum of *N*-(1- naphthyl) methylene *N, N* dimethyl chitosan chloride (1:4) is shown in Figure 4.20.

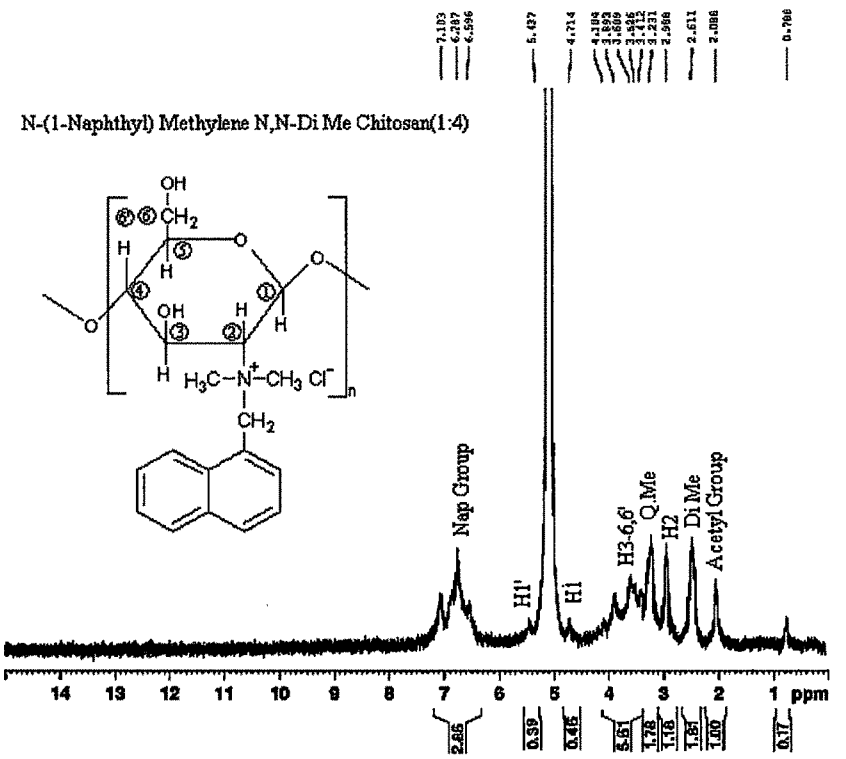



**Figure 4.20** $^1$HNMR spectrum of *N*-(1- naphthyl) methylene *N, N* dimethyl chitosan chloride (1:4)

Various peaks (δ) with corresponding integrals (I) for N-Np Q CHT (1:4) depicted by $^1$HNMR and the DQ % calculated from the expression 4.12 are summarized as below.

$\delta_{Ar}$= 6.596-  $I_{Ar}$ = 2.86  Seven protons (7H) of aromatic group.

7.103 ppm

| | | |
|---|---|---|
| n = 7 | | Aromatic protons. |
| $\delta_{NAc}$ =2.088 ppm | $I_{NAc}$ = 1.0 | Three protons (3H) methyl terminal of acetyl group, -N-CO-$CH_3$ |
| $\delta_{H2}$ = 2.988 ppm | $I_{H2}$ = 1.18 | One proton (1H) bound to C2 glucosamine (GlcN) residue. |
| $\delta_{H3\text{-}6,6'}$ = 3.3-4.5 | $I_{H3\text{-}6,6'}$ = 5.61 | Five protons (5H) bounded to C-3,4,5,6 & 6' of GlcN. |
| $\delta_{QMe}$ = 3.231 | $I_{QMe}$ = 1.78 | Six protons (6H) of two methyl groups attached to N-dodecyl substituted of GlcN residue. |
| $\delta_{(DiMe)}$ =2.611 | $I_{DiMe}$ = 1.81 | Six protons (6H) of two methyl groups attached to free amino groups of GlcN residue. |
| $\delta_{(H1')}$ = 4.714 | $I_{H1}$ = 0.46 | One anomeric proton (1H)of the glucosamine units |
| $\delta_{(H1)}$ = 5.437 | $I_{H1'}$ = 0.39 | One anomeric proton (1H) of the N-acetyl glucosamine units |

DS =**37.6 %, DQ = 34.9 %**

#### *4.3.1.3.4 Elemental analysis*

The degree of substitution (DS) of N- Benzyl CHT (1:4) and N-(1- Naphthyl) Methylene CHT was determined from C/N value of elemental analysis using the formula 4.9.

$$\frac{C1}{N1} \times (1 - DS) + \frac{C2}{N2} \times DS = \frac{C3}{N3} DAC \qquad \textbf{(4.9)}$$

Where, C1/N1 is calculated from the formula of non substituted CHT i.e. glucosamine residue (GlcN), C2/N2 from the N-Substituted residue and C3/N3 is found value of sample by elemental analysis. DAC is degree of deacetylation, 0.9 (i.e.90 %.).The percentage CHN content of selected chitosan derivatives determined by the elemental analysis is presented in Table 4.13 and the evaluated DS values of these derivatives in Table 4.19. The calculations are illustrated as follows.

Calculations:

*N- Benzyl chitosan (1:4) [N-Bz CHT (1:4)]*

$$\frac{C1}{N1}\times(1-DS)+\frac{C2}{N2}\times DS=\frac{C3}{N3}DAC$$

$$5.14\times(1-DS)+11.14\times DS=8.53\times0.9$$

DS = 0.4228 unit/GlcN residue OR **42.3 %**

*N-(1-Naphthyl) methylene Chitosan (1:4) [N-NpCHT(1:4])*

$$\frac{C1}{N1}\times(1-DS)+\frac{C2}{N2}\times DS=\frac{C3}{N3}DAC$$

$$5.14\times(1-DS)+14.57\times DS=9.36\times0.9$$

DS = 0.3483 unit/GlcN residue OR **34.8 %**

***4.3.1.3.5 Conductometric titrations***

Degree of quaternization of quaternized N-alkyl chitosan chloride derivatives were also determined conductometrically by the titration against 0.1M $AgNO_3$ using the expression 4.1 as discussed earlier in section 4.3.1.1.3.

$$DQ\,(\%)=\frac{M_Q\times V\times[AgNO_3]}{m}X100 \qquad \textbf{(4.1)}$$

Where,

$M_Q$ is the molecular weight of repeating unit of the sample containing quaternized site, these values were obtained from the respective structural formula of derivatives given in Table 4.12. V and [$AgNO_3$] are the equivalent volume in litre and concentration of $AgNO_3$ aqueous solution (0.1M) respectively and *m* (g) is the mass of the sample which was 0.5g. The conductometric titration data for *N*-Bz Q CHT(1:2), *N*-Bz Q CHT (1:4) and *N*-Np Q CHT (1:4) are presented in Table 4.17 and the evaluated DQ values for the derivatives in Table 4.18 and Table 4.19.

**Table 4.17** Conductometric titrations for *N*-aryl Q CHT derivatives

| $AgNO_3$ (0.1M) | Conductance, mMhos | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | N-Bz Q CHT (1:2) | | | N-Bz Q CHT (1:4) | | | N-Np Q CHT (1:4) | | |
| | I | II | III | I | II | III | I | II | III |
| 0 | 3.90 | 3.90 | 3.90 | 4.00 | 4.00 | 3.90 | 3.70 | 3.70 | 3.75 |
| 0.5 | 3.75 | 3.80 | 3.85 | 3.90 | 3.90 | 3.80 | 3.50 | 3.60 | 3.65 |
| 1.0 | 3.55 | 3.55 | 3.60 | 3.75 | 3.70 | 3.75 | 3.25 | 3.45 | 3.40 |
| 1.5 | 3.35 | 3.35 | 3.40 | 3.50 | 3.50 | 3.70 | 3.30 | 3.25 | 3.25 |
| 2.0 | 3.25 | 3.25 | 3.30 | 3.35 | 3.40 | 3.50 | 2.80 | 2.80 | 3.00 |
| 2.5 | 3.00 | 3.00 | 3.10 | 3.25 | 3.20 | 3.25 | 2.60 | 2.85 | 2.90 |
| 3.0 | 2.80 | 2.90 | 2.90 | 3.10 | 3.15 | 3.10 | 2.50 | 2.75 | 2.75 |
| 3.5 | 2.75 | 2.75 | 2.85 | 3.00 | 3.00 | 2.90 | 2.25 | 2.50 | 2.45 |
| 4.0 | 2.65 | 2.70 | 2.70 | 2.80 | 2.75 | 2.80 | 2.00 | 2.25 | 2.25 |
| 4.5 | 2.40 | 2.50 | 2.40 | 2.75 | 2.70 | 2.80 | 1.80 | 2.00 | 1.90 |
| 5.0 | 2.25 | 2.25 | 2.30 | 2.50 | 2.50 | 2.55 | 1.75 | 1.90 | 1.90 |
| 5.5 | 2.25 | 2.25 | 2.25 | 2.50 | 2.40 | 2.45 | 1.70 | 1.85 | 1.85 |
| 6.0 | 2.10 | 2.10 | 2.15 | 2.35 | 2.40 | 2.35 | 2.00 | 2.00 | 2.10 |
| 6.5 | 1.90 | 2.00 | 2.00 | 2.25 | 2.30 | 2.25 | - | - | - |
| 7.0 | 2.25 | 2.20 | 2.25 | 2.15 | 2.30 | 2.35 | 2.70 | 2.60 | 2.60 |
| 7.5 | 2.50 | 2.55 | 2.50 | 2.75 | 2.70 | 2.75 | - | - | - |
| 8.0 | 2.85 | 2.85 | 2.85 | 3.00 | 3.00 | 3.00 | 3.50 | 3.85 | 3.85 |
| 9.0 | 3.50 | 3.50 | 3.50 | 3.80 | 3.85 | 3.75 | 4.25 | 4.15 | 4.10 |
| 10.0 | 4.25 | 4.25 | 4.25 | 4.50 | 4.60 | 4.60 | 4.90 | 5.00 | 5.00 |
| 11.0 | 5.00 | 5.00 | 4.90 | 5.40 | 5.40 | 5.35 | 5.00 | 4.20 | 5.25 |
| 12.0 | 5.75 | 5.75 | 5.70 | 6.25 | 6.20 | 6.30 | 6.40 | 6.50 | 6.50 |
| 13.0 | 6.40 | 6.40 | 6.35 | 6.90 | 6.90 | 7.00 | 7.25 | 7.25 | 7.25 |
| 14.0 | 7.15 | 7.20 | 7.25 | 7.70 | 7.75 | 7.75 | 7.80 | 7.90 | 8.00 |

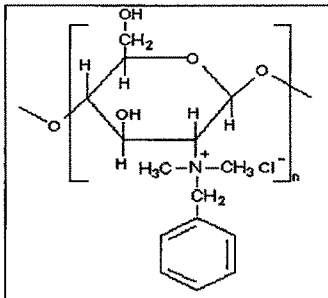
*CHT: $CH_3I$ (1:15), CHT: NaOH (1:2)*

**Table 4.18** Conductometric method for determination DQ of *N*-aryl Q CHT derivatives

| Sample | 0.1M $AgNO_3$ titrant (V), ml | | | | DQ, % |
|---|---|---|---|---|---|
| | I | II | III | Average | |
| N-Bz Q CHT (1:2) | 6.6 | 6.6 | 6.8 | 6.66 | 42.07 |
| N-Bz Q CHT (1:4) | 6.6 | 6.6 | 6.5 | 6.56 | 41.44 |
| N-Np Q CHT (1:4) | 5.4 | 6.6 | 6.4 | 6.47 | 39.96 |

*CHT:$CH_3I$=1:15, CHT: NaOH =1:2*

*DQ of N-benzyl N, N dimethyl chitosan chloride (1:4) [Q-Bz CHT(1:4)]*



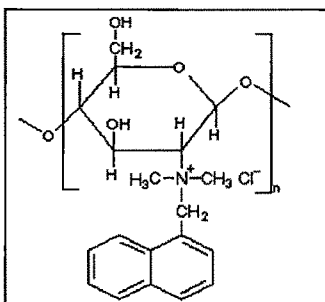
| | |
|---|---|
| C,15 X 12 = | 180 |
| O, 4 X 16 = | 64 |
| H, 22 X 1 = | 22 |
| N,1 X 14 = | 14 |
| Cl,1X 35.5 = | 35.5 |
| $M_Q$ = | 315.5 |

$M_Q$ = 315.5, m= 0.5 g, V = 6.6, 6.6, 6.5 = 6.57 ml or V= 0.00657 L

$$DQ\ (\%) = \frac{M_Q \times V \times [AgNO_3]}{m} X100$$

$$DQ\ (\%) = \frac{315.5 \times 0.00657 \times 0.1}{0.5} X100 = \mathbf{41.44\ \%}$$

*N-(1-Naphthyl) methylene N, N-dimethyl chitosan chloride(1:4)[N-NpQCHT(1:4)]*



| | |
|---|---|
| C,19 X 12 = | 228 |
| O, 4 X 16 = | 64 |
| H, 24 X 1 = | 24 |
| N,1 X 14 = | 14 |
| Cl,1X 35.5= | 35.5 |
| $M_Q$ = | 365.5 |

$M_Q$ = 365.5, m =0.5 g, V = 5.4, 6.6, 6.4 = 6.47 ml or V= 0.00647 L

$$DQ\ (\%) = \frac{M_Q \times V \times [AgNO_3]}{m} X100$$

$$= \frac{315.5 \times 0.00647 \times 0.1}{0.5} X100 = \mathbf{40\ \%}$$

**Table 4.19** DS and DQ of *N*-substituted CHT

| *N*- Alkyl/Aryl CHT | | | *N*- Alkyl/Aryl Q CHT | | |
|---|---|---|---|---|---|
| **Sample** | **Degree of substitution (DS), %** | | **Sample** | **Degree of quaternization (DQ), %** | |
| | **$H^1$NMR analysis** | **C/N analysis** | | **$H^1$NMR analysis** | **Conductometry** |
| N-Et CHT (1:2) | 45.5 | 47.6 | N- Et Q CHT (1:2) | 46.3 | 52.0 |
| N-Et CHT (1:4) | 82.6 | - | N- Et Q CHT (1:4) | - | 52.2 |
| N-Bu CHT (1:2) | 40.1 | 43.3 | N- Bu Q CHT (1:2) | 43.0 | 47.5 |
| N-Bu CHT (1:4) | 71.2 | - | N- Bu Q CHT (1:4) | - | 41.0 |
| N-Dod CHT (1:2) | 22.1 | - | N- Dod Q CHT (1:2) | - | 46.4 |
| N-Dod CHT (1:4) | 37.6 | 39.3 | N-Dod Q CHT (1:4) | 40.8 | 45.1 |
| N-Bz CHT (1:2) | 17.5 | - | N-Bz Q CHT (1:2) | - | 42.1 |
| N-Bz CHT (1:4) | 45.0 | 42.3 | N-Bz Q CHT (1:4) | 34.0 | 41.4 |
| N-Np CHT(1:4) | 37.6 | 34.8 | N-Np Q CHT(1:4) | 35.0 | 40.0 |

*The value in parentheses indicate the CHT: CHO ratio,*
*The N- Alkyl/Aryl CHT were quaternized with $CH_3I$ at fifteen fold excess*

The DS and DQ determined using different analytical techniques for *N*-alkylated and *N*-arylated CHT and their quaternized derivatives are summarized in Table 4.19. It can be observed from the table that data obtained from different methods are quite nearer. The DQ determined by conductometry were found to be somewhat higher than that determined by $^1$HNMR spectroscopy. This may be due to the presence of extra chloride ions associated with mono-, di- and trimethylated amino sites generated during quaternization reaction; and also to the presence of unbound chloride ions that was not completely removed during purification process of samples. Nevertheless, the conductometric titration methods are useful tool for the determination of DQ of quaternized samples since the same trend of $^1$HNMR was followed. Further it was observed that the DS of *N*-aryl CHT derivatives determined by $^1$HNMR method were higher than the results of elemental analysis. On the other hand, the trend was reversed in

case of *N*-alkyl CHT derivatives. In the spectrum of *N*-aryl derivatives, the aromatic proton resonances appear in the downfield region i.e. left to the $D_2O$ signal, mostly in $\delta$ = 6 to 7 ppm, compared to the residual sugar protons and therefore they can be integrated with minimal interference. While, the signals due to protons bonded to *N*-alkyl groups appear together with signals of protons of saccharide i.e. in the region of $\delta$ <4.5 leading to many superimpositions. It is worthwhile to consider the $^1$HNMR methodology as a more authentic for aryl derivatives.

It was also observed from the Table 4.19 that degree of alkylation for a given alkyl chain, as for example N-Et CHT, increased with concentration of aldehyde. However, at a given concentration of aldehyde the degree of substitution decreased with increase in chain length. Further, aromatic aldehydes were less effective substituent to form Schiff's base compared to the aliphatic aldehydes. In general, smaller size and aliphatic aldehydes are more effective substituents while bigger size and aromatic aldehydes give poor degree of substitution on chitosan. When these *N*-substituted CHT derivatives were further quaternized with methyl iodide, the degree of quaternization was also decreased with increase in molecular size of the alkyl/aryl substituents. As discussed earlier, the reaction of chitosan with aldehyde proceeds through electrophilic substitution reaction in which the carbonyl carbon of aldehyde, the electron deficient i.e. electrophile, reacts with nucleophilic amino group of chitosan. Thus for maximum reactivity towards nucleophiles, the carbonyl carbon should be as +ve as possible and not sterically hindered by adjacent groups. The alkyl groups attached to carbonyl carbon being electron releasing decreases the positivity of the carbon atom and also the bulky alkyl groups offer steric hindrance to the approaching amino group of chitosan. Thus, besides steric hindrance, with increase in alkyl chain length the reactivity of aldehyde is decreased and resulted into poor degree of substitution. In case of aromatic aldehydes the $\alpha$-H is not involved in the reaction and the conjugation of carbonyl carbon with aryl ring reduces the electrophilic reactivity due to delocalized $\pi$-electrons. Hence aromatic aldehydes are less reactive than their aliphatic counterpart. This steric hindrance is also responsible for the decrease in quaternization with increase in molecular size of substituents.

### 4.3.2 Viscosity behavior of *N*- substituted CHT derivatives

Besides the estimation of molecular weight, the viscosity measurement data of polymer solutions are useful in studying the chain conformation. Various factors such as temperature, pH, electrolytes, molecular weight, polymer concentration, nature of counter ion etc are found to influence the conformational arrangements of poly electrolytes chains in aqueous solutions and also the viscosity [67]. Effect of quaternization of CHT and *N*-alkyl and *N*-aryl CHT derivatives on their viscosity behaviour and the intrinsic viscosity [η], a function of molecular weight, was evaluated. The solutions were prepared in acetic acid / sodium acetate solvent system with corresponding concentration of 0.25 M / 0.25 M recommended for the determination of molecular weight of chitosan using Mark-Houwink equation [68]. The average of three readings of flow time of various *N*-substituted Q CHT derivative solutions of different concentrations, in presence and absence of sodium acetate, are presented in Table 4.20 and Table 4.22 respectively. The reduced viscosities ($\eta_{red}$) [69] calculated from these readings using equations 2.7, 2.8 and 2.9(chapter 2) for polymeric solutions in presence and absence of sodium acetate are presented in Table 4.21 and Table 4.23 respectively and graphically in Figures 4.21, 4.22 and 4.23. The intrinsic viscosities obtained by extrapolation of these curves to intercept Y-axis of zero concentration are given in Table 4.24 and Figure 4.24.

**Table 4.20** Viscometer readings of *N*- sub CHT solutions in presence of sodium acetate

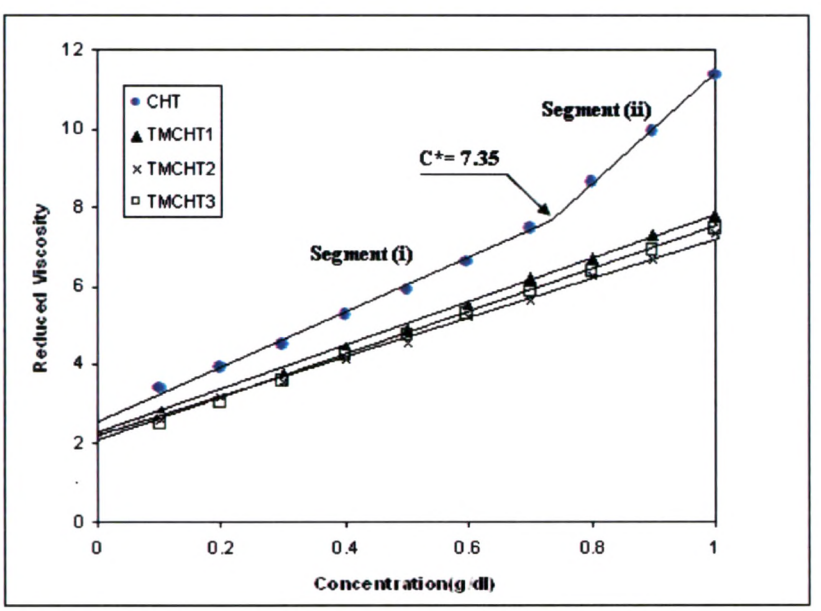
| Conc, g/dl | Average flow time (T), seconds | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | CHT | TMCHT 1 | TMCHT 2 | TMCHT 3 | N-Et Q CHT (1:2) | N-Bu Q CHT (1:2) | N-Dod Q CHT (1:4) | N-Bz QCHT (1:4) | N-Np QCHT (1:4) |
| 0.1 | 21.27 | 20.28 | 19.98 | 19.74 | 19.76 | 20.16 | 20.41 | 20.20 | 20.03 |
| 0.2 | 28.27 | 26.22 | 25.96 | 25.33 | 25.96 | 26.34 | 27.11 | 26.66 | 26.79 |
| 0.3 | 37.23 | 33.72 | 32.87 | 32.87 | 33.44 | 34.15 | 35.87 | 36.44 | 36.01 |
| 0.4 | 49.14 | 43.80 | 42.21 | 42.53 | 43.36 | 44.94 | 47.80 | 46.09 | 47.67 |
| 0.5 | 62.61 | 54.59 | 51.89 | 53.48 | 54.91 | 56.81 | 60.70 | 59.91 | 59.04 |
| 0.6 | 78.69 | 68.24 | 65.09 | 65.96 | 72.05 | 68.24 | 76.24 | 70.91 | 75.10 |
| 0.7 | 98.32 | 84.75 | 78.52 | 80.97 | 84.19 | 88.63 | 96.30 | 91.41 | 92.52 |
| 0.8 | 125.28 | 100.81 | 95.22 | 96.62 | 100.93 | 108.93 | 115.15 | 111.47 | 113.76 |
| 0.9 | 157.41 | 120.28 | 111.57 | 114.28 | 119.42 | 127.42 | 140.13 | 131.28 | 143.13 |
| 1.0 | 196.00 | 139.66 | 132.52 | 133.94 | 142.04 | 150.77 | 162.19 | 156.00 | 163.46 |

*Solvent: Acetic acid =0.25M, Sodium acetate = 0.25M, $T_0$= 15.87 sec, Temp 30 $^0C$*

**Table 4.21** Reduced viscosity ($\eta_{red}$) of *N*-sub CHT solutions in presence of sodium acetate

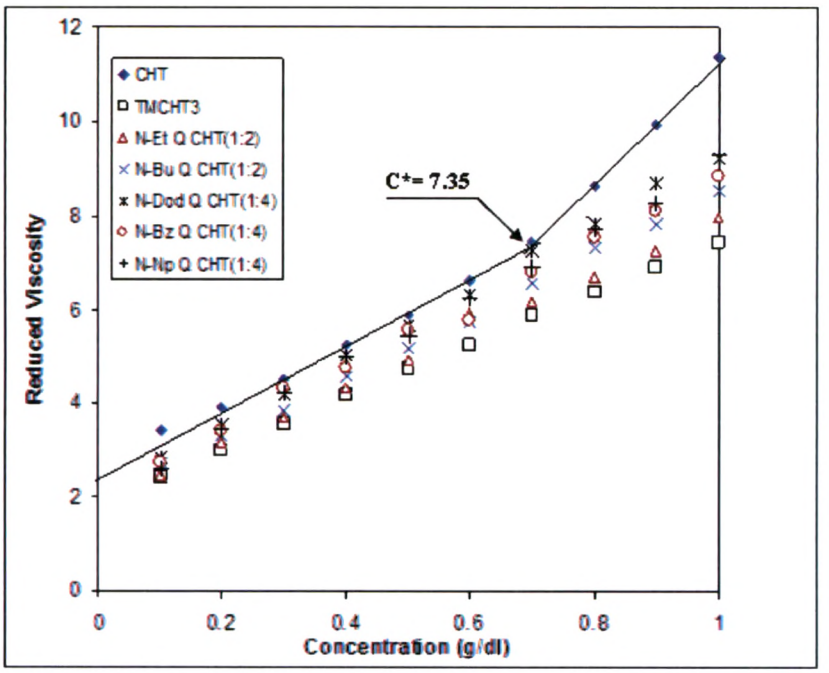
| Conc, g/dL | Reduced Viscosity ($\eta_{red}$) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | CHT | TMCHT 1 | TMCHT 2 | TMCHT 3 | N-Et Q CHT (1:2) | N-Bu Q CHT (1:2) | N-Dod Q CHT (1:4) | N-Bz QCHT (1:4) | N-Np QCHT (1:4) |
| 0.1 | 3.40 | 2.78 | 2.59 | 2.44 | 2.45 | 2.70 | 2.86 | 2.73 | 2.62 |
| 0.2 | 3.91 | 3.26 | 3.18 | 2.98 | 3.18 | 3.30 | 3.54 | 3.40 | 3.44 |
| 0.3 | 4.49 | 3.75 | 3.57 | 3.57 | 3.69 | 3.84 | 4.20 | 4.32 | 4.23 |
| 0.4 | 5.24 | 4.40 | 4.15 | 4.20 | 4.33 | 4.58 | 5.03 | 4.76 | 5.01 |
| 0.5 | 5.89 | 4.88 | 4.54 | 4.74 | 4.92 | 5.16 | 5.65 | 5.55 | 5.44 |
| 0.6 | 6.60 | 5.50 | 5.17 | 5.26 | 5.90 | 5.74 | 6.34 | 5.78 | 6.22 |
| 0.7 | 7.42 | 6.20 | 5.64 | 5.86 | 6.15 | 6.55 | 7.24 | 6.80 | 6.90 |
| 0.8 | 8.62 | 6.69 | 6.25 | 6.36 | 6.70 | 7.33 | 7.82 | 7.53 | 7.71 |
| 0.9 | 9.91 | 7.31 | 6.70 | 6.89 | 7.25 | 7.81 | 8.70 | 8.08 | 8.28 |
| 1.0 | 11.35 | 7.80 | 7.35 | 7.44 | 7.95 | 8.50 | 9.22 | 8.83 | 9.30 |

*Solvent: Acetic acid =0.25M, Sodium Acetate = 0.25M, $T_0$= 15.87 sec, DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40*




*DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9*

**Figure 4.21** Reduced viscosity ($\eta_{red}$) TMCHT solutions in presence of sodium acetate




*DQ (%):TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 45/41.4, N-Np Q CHT(1:4)= 37.6/40*

**Figure 4.22** Reduced viscosity ($\eta_{red}$) *N*- sub CHT solutions in presence of sodium acetate

**Table 4.22** Viscometer readings of *N*- sub CHT solutions in absence of sodium acetate

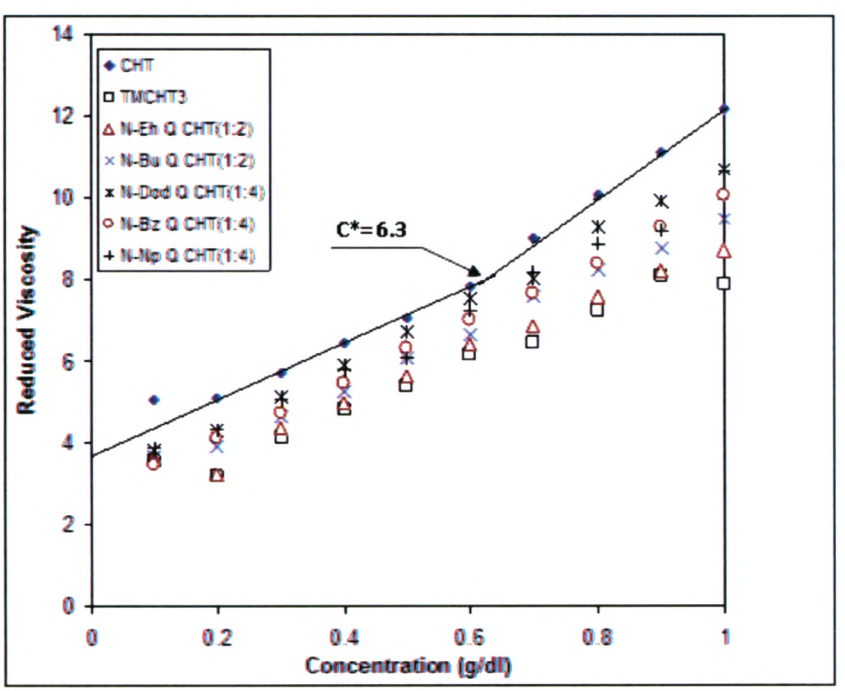
| Conc, g/dL | Average flow time, sec | | | | | | |
|---|---|---|---|---|---|---|---|
| | CHT | TMCHT3 | N-Et QCHT (1:2) | N-Bu QCHT (1:2) | N-Dod QCHT (1:4) | N-Bz QCHT (1:4) | N-Np QCHT (1:4) |
| 0.1 | 23.67 | 21.33 | 21.44 | 21.53 | 21.77 | 21.17 | 21.85 |
| 0.2 | 31.79 | 25.75 | 25.88 | 28.05 | 29.34 | 28.68 | 29.28 |
| 0.3 | 42.56 | 35.15 | 36.33 | 37.60 | 40.01 | 38.12 | 39.63 |
| 0.4 | 56.35 | 45.96 | 46.97 | 48.92 | 53.01 | 50.12 | 52.13 |
| 0.5 | 71.22 | 58.16 | 59.81 | 63.51 | 68.71 | 64.48 | 63.59 |
| 0.6 | 89.69 | 73.63 | 75.99 | 78.35 | 86.95 | 81.85 | 84.11 |
| 0.7 | 114.90 | 86.37 | 91.10 | 99.04 | 104.10 | 100.14 | 106.09 |
| 0.8 | 142.29 | 107.03 | 110.81 | 119.12 | 132.34 | 121.26 | 127.43 |
| 0.9 | 173.27 | 130.48 | 132.18 | 139.83 | 156.41 | 147.06 | 146.07 |
| 1.0 | 207.14 | 139.77 | 152.68 | 164.96 | 184.16 | 173.93 | 183.53 |

*Solvent: Acetic acid =0.25M, $T_0$= 15.74 sec, DQ (%): TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) =40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40*

**Table 4.23** Reduced viscosity ($\eta_{red}$) of *N*- sub CHT solutions in absence of sodium acetate

| Conc, g/dL | Reduced Viscosity ($\eta_{red}$) | | | | | | |
|---|---|---|---|---|---|---|---|
| | CHT | TMCHT3 | N-Et QCHT (1:2) | N-Bu QCHT (1:2) | N-Dod QCHT (1:4) | N-Bz QCHT (1:4) | N-Np QCHT (1:4) |
| 0.1 | 5.04 | 3.55 | 3.62 | 3.68 | 3.83 | 3.45 | 3.88 |
| 0.2 | 5.10 | 3.18 | 3.22 | 3.91 | 4.32 | 4.11 | 4.30 |
| 0.3 | 5.68 | 4.11 | 4.36 | 4.63 | 5.14 | 4.74 | 5.06 |
| 0.4 | 6.45 | 4.80 | 4.96 | 5.27 | 5.92 | 5.46 | 5.78 |
| 0.5 | 7.05 | 5.39 | 5.60 | 6.07 | 6.73 | 6.32 | 6.08 |
| 0.6 | 7.83 | 6.13 | 6.38 | 6.63 | 7.54 | 7.00 | 7.24 |
| 0.7 | 9.00 | 6.41 | 6.84 | 7.56 | 8.02 | 7.66 | 8.20 |
| 0.8 | 10.05 | 7.25 | 7.55 | 8.21 | 9.26 | 8.38 | 8.87 |
| 0.9 | 11.12 | 8.10 | 8.22 | 8.76 | 9.93 | 9.27 | 9.20 |
| 1.0 | 12.16 | 7.88 | 8.70 | 9.48 | 10.70 | 10.05 | 10.66 |

*Solvent: Acetic acid =0.25M, $T_0$= 15.74 sec, 30 $^0$C, DQ (%):TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40*



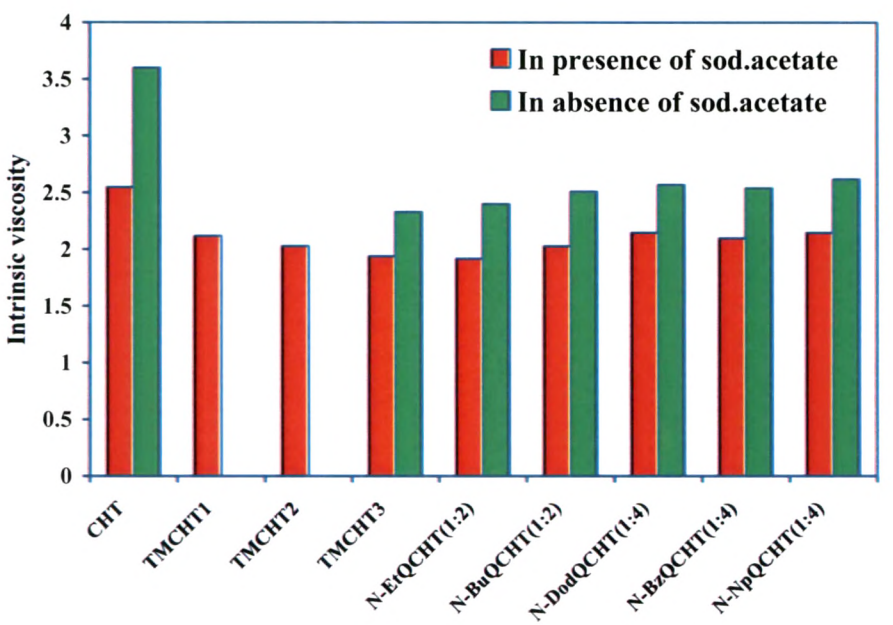

*DQ (%):TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 45/41.4, N-Np Q CHT(1:4)= 37.6/40*

**Figure 4.23** Reduced viscosity ($\eta_{red}$) *N*- sub CHT solutions in absence of sodium acetate

**Table 4.24** Effect of quaternization on intrinsic viscosity of CHT derivatives

| Sample | In presence of Sodium Acetate | | In absence of Sodium Acetate | | Drop in [η] due to sodium acetate, % |
|---|---|---|---|---|---|
| | Intrinsic viscosity [η] | Slope | Intrinsic viscosity [η] | Slope | |
| CHT | 2.55 | *(i) 6.85 (ii)13.13 | 3.60 | (i) 7.23 (ii) 12.42 | 29.1 |
| TMCHT1 | 2.12 | 5.65 | - | - | - |
| TMCHT2 | 2.03 | 5.23 | - | - | - |
| TMCHT3 | 1.94 | 5.51 | 2.33 | 6.08 | 16.7 |
| N Et Q CHT(1:2) | 1.92 | 6.00 | 2.40 | 6.40 | 20.0 |
| N Bu Q CHT(1:2) | 2.03 | 6.48 | 2.51 | 6.99 | 19.1 |
| N Dod Q CHT(1:4) | 2.15 | 7.15 | 2.57 | 8.07 | 17.0 |
| N Bz Q CHT(1:4) | 2.10 | 6.37 | 2.54 | 7.30 | 17.3 |
| N Np Q CHT(1:4) | 2.15 | 6.87 | 2.62 | 7.71 | 17.9 |

** Segments of the curve i.e. Segment (i) and Segment (ii)DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 45/41.4, N-Np Q CHT(1:4)= 37.6/40*




*DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40*

**Figure 4.24** Effect of quaternization on intrinsic viscosity of CHT derivatives

The intrinsic viscosity, as observed from Table 4.24 and Figure 4.24, was dropped due to quaternization process indicating a depolymerization of parent chitosan. The drop in viscosity was substantial even at low concentrations of methyl iodide (i.e. at lower DQ) and was very slightly affected with further increase in methyl iodide concentration. This means the depolymerization of CHT occurred is not only attributed to the extent of quaternization but also to the reaction condition such as duration, temperature and the presence of ingredients i.e. sodium hydroxide and NMP. At almost similar levels of DS and DQ of *N*-substituted Q CHT derivatives, the intrinsic viscosity was found to be slightly increased with increase in chain length or molecular size of substituent. Presence of electrolyte i.e. sodium acetate in CHT derivative solutions reduced the intrinsic viscosity. The loss in viscosity was maximum of CHT solution and minimum of TMCHT3 solution. This apparent change in [η] due to electrolyte in solvent, however, does not mean the change in molecular weight of same sample in two different solvent systems, the Mark-Houwink constants α and K that actually change and not the molecular weight.

The curves for TMCHT in Figure 4.21 were found to be almost linear without any point of inflection or critical concentration (C*), apparently indicating scattered distribution of polymer molecules without aggregation. Such critical concentrations (C*) were observed in CHT solutions. When the curves for these polymer solutions were studied in absence of electrolyte (sodium acetate), Figure 4.23, some irregularities noticed. The position of C* for CHT solution was shifted left to 6.3 g/dL. TMCHT, here again, did not show any point of critical concentration but showed slight increased viscosity at high dilution/low concentration of paradoxical behaviour often observed in polyelectrolytes. The increased viscosity of poly cations at high dilutions may be attributed to the chain expansions due to electrostatic repulsion between same ions on macromolecule [58,66,70]. In presence of added electrolyte (sodium acetate), the charges will be screened and consequently the polyelectrolyte chain will adopt coiled conformation as demonstrated in Figure 4.25. Further these added electrolyte ions offer shielding effect to cause polymer molecules repel each other resulting into decreased viscosity [71]. Regardless the downward influence of depolymerization of CHT due to quaternization reaction and also due to the presence of electrolyte on viscosity, a

contradictory i.e. increase in viscosity of modified CHT is expected due to the introduction of bulkier side groups. The loss in molecular weight due to depolymerization during quaternization reaction is believed to overcome to some extent due to introduced side methyl groups that offer resistance to flow/slippages of molecules. It means the viscosity of TMCHT is governed by two opposite phenomena namely the fall in viscosity due to depolymerization during quaternization reaction and shielding effect of electrolytes; and the increase in viscosity due attached bulky methyl groups.

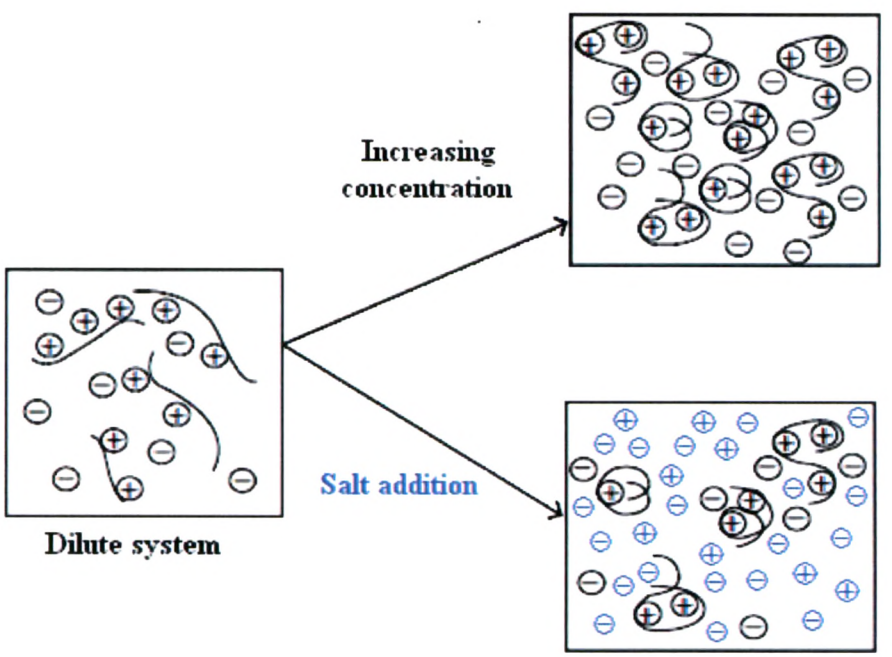



**Figure 4.25** Polycations chain conformation as a function of polymer concentration and electrolyte

At about similar DS values of *N*- substituted Q CHT derivatives, the effect of molecular size of *N*-substituent on intrinsic viscosity was very much close to that of TMCHT derivatives nevertheless with some increased trend as shown in Table 4.24. It was observed from Figure 4.22 that the curves for all quaternized N-substituted CHT derivative solutions containing sodium acetate were almost linear without any inflections of critical concentrations (C*). The *N*- substituted Q CHT derivatives showed increased viscosities at higher concentrations as a function of chain length of substituent. The

resistance to flow or slippages of macromolecules may occur due to bulkier side groups and intra and inter molecular hydrophobic-hydrophobic interactions [72]. The possibility of contribution of aggregation of polyelectrolyte molecules at higher concentrations to viscosity is meager due to ionic repulsion but cannot be completely discarded. While comparing the influence of added electrolyte on chain conformation of *N*-substituted Q CHT derivatives, Figures 4.22, 4.23 and 4.24 envisage that the influence was maximum in CHT and lower CHT derivatives solutions where as it was nominal in solutions of higher substituted derivatives. In other words, the charge screening on quaternized sites was subdued due the chain length or molecular size of *N*-alkyl or *N*-aryl substituent.

### 4.3.3 Treatment of cotton fabric with *N*-substituted CHT derivatives

Chitosan and its *N*-substituted derivatives namely *N, N, N* -trimethyl chitosan chloride (TMCHT), *N*-alkyl chitosan and *N*-aryl chitosan and their quaternized derivatives, enumerated in Table 4.12, were applied on cotton fabric by conventional pad-dry-cure method. TMCHT of different DQ and *N*-alkyl/*N*-aryl CHT derivatives of almost similar DS and DQ respectively was selected for textile application. Concentrations of these derivatives for pad bath application are mentioned in Table 4.25.

**Table 4.25** Application of *N*-sub CHT compounds on cotton fabric

| ***N*-Alkyl/Aryl CHT** | | ***N*- Alkyl/Aryl Q CHT** | | **Conc in pad bath, g/L** | | |
|---|---|---|---|---|---|---|
| **Sample** | **DS, %** | **Sample** | **DQ, %** | | | |
| Control | - | - | - | - | - | - |
| CHT | - | - | - | 2.5 | 5 | 10 |
| - | - | TMCHT1 | 13.4 | 2.5 | 5 | 10 |
| - | - | TMCHT2 | 22.0 | 2.5 | 5 | 10 |
| - | - | TMCHT3 | 50.9 | 2.5 | 5 | 10 |
| N-Et CHT (1:2) | 45.5 | N-Et Q CHT (1:2) | 51.7 | 2.5 | 5 | 10 |
| N-Bu CHT (1:2) | 40.1 | N-Bu Q CHT (1:2) | 47.5 | 2.5 | 5 | 10 |
| N-Dod CHT(1:4) | 37.6 | N-Dod Q CHT (1:4) | 45.1 | 2.5 | 5 | 10 |
| N-Bz CHT (1:4) | 45.0 | N-Bz Q CHT (1:4) | 41.4 | 2.5 | 5 | 10 |
| N-Np CHT(1:4) | 37.6 | N-NpQ CHT (1:4) | 40.0 | 2.5 | 5 | 10 |

Since the treated fabric samples were evaluated in many cases using optical instruments, any changes in fabric construction due to above treatments may lead to

variations in results. In order to minimize the error, a blank treatment to the fabric was also given during the padding of other samples, this samples was termed as 'control' sample with which the results of treated samples were compared as discussed in section 2.3.11, chapter 2.

### *4.3.3.1 Effect of N- substituted CHT treatment on appearance of cotton fabric*

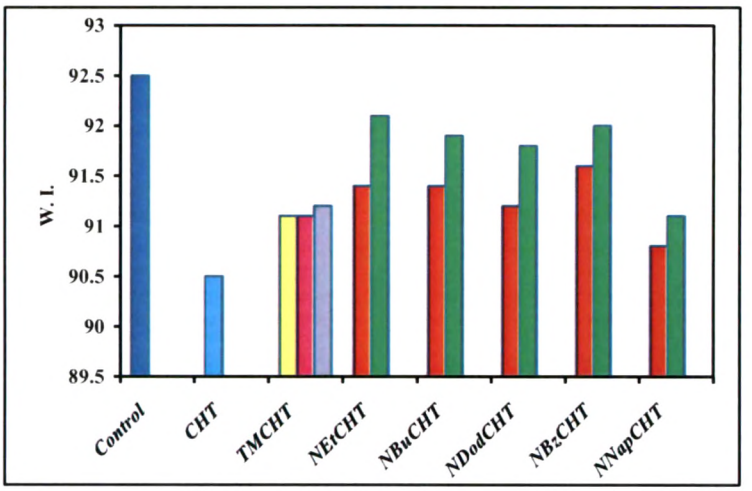
Analogous to the chitosan treatment, *N*- modified chitosans are believed to alter the surface characteristics of cotton fabrics. In context to this phenomenon, the CHT and *N*-substituted CHT derivatives treated cotton fabrics were evaluated for the whiteness, yellowness and brightness indices on computer colour matching system. The results are presented in Table 4.26 and Table 4.27 and in Figures 4.26, 4.27 & 4.28.

**Table 4.26** Effect of *N*-Alkyl/Aryl CHT treatment on appearance of cotton fabric

| Sample | DS, % | Conc in pad bath, g/L | Indices | | |
|---|---|---|---|---|---|
| | | | WI | YI | BI |
| Control | - | - | 92.5 | 2.6 | 84.6 |
| CHT | - | 2.5 | 90.9 | 3.3 | 81.6 |
| | | 5 | 90.8 | 3.4 | 81.4 |
| | | 10 | 90.5 | 4.7 | 80.6 |
| N-Et CHT (1:2) | 45.5 | 2.5 | 91.4 | 3.3 | 82.4 |
| | | 5 | 90.9 | 3.3 | 81.6 |
| | | 10 | 91.4 | 3.4 | 82.4 |
| N-Bu CHT (1:2) | 40.1 | 2.5 | 91.5 | 3.7 | 80.5 |
| | | 5 | 91.8 | 3.3 | 82.6 |
| | | 10 | 91.4 | 3.3 | 82.4 |
| N-Dod CHT (1:4) | 37.6 | 2.5 | 90.6 | 4.7 | 80.6 |
| | | 5 | 91.1 | 3.5 | 82.5 |
| | | 10 | 91.2 | 3.1 | 83.3 |
| N-Bz CHT (1:4) | 45.0 | 2.5 | 91.8 | 2.8 | 83.1 |
| | | 5 | 91.7 | 3.3 | 82.6 |
| | | 10 | 91.6 | 3.5 | 82.5 |
| N-Np CHT (1:4) | 37.6 | 2.5 | 91.8 | 2.8 | 83.1 |
| | | 5 | 91.4 | 3.4 | 82.4 |
| | | 10 | 90.8 | 3.4 | 81.4 |

**Table 4.27** Effect of *N*-Alkyl/Aryl Q CHT derivatives treatment on appearance of cotton fabric

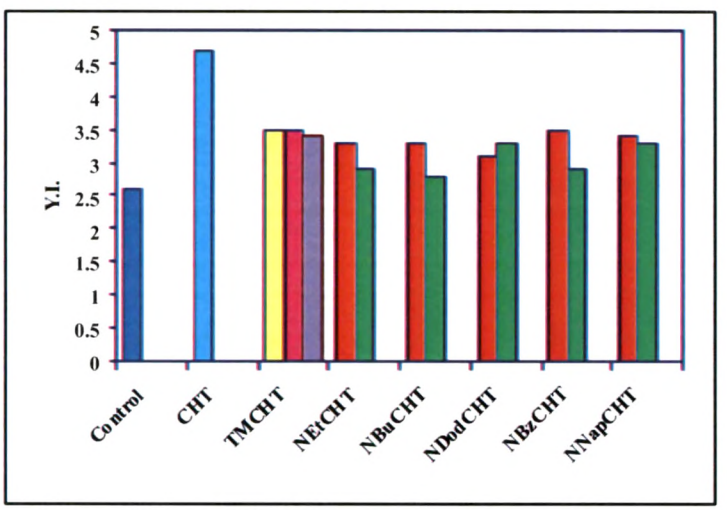
| Sample | DQ, % | Conc in pad liquor, g/L | Indices | | |
|---|---|---|---|---|---|
| | | | WI | YI | BI |
| Control | - | - | 92.5 | 2.6 | 84.6 |
| CHT | - | 2.5 | 90.9 | 3.3 | 81.6 |
| | | 5 | 90.8 | 3.4 | 81.4 |
| | | 10 | 90.5 | 4.7 | 80.6 |
| TMCHT1 | 13.4 | 2.5 | 92.0 | 2.811 | 83.0 |
| | | 5 | 91.2 | 3.286 | 82.1 |
| | | 10 | 91.1 | 3.5 | 82.5 |
| TMCHT 2 | 22.0 | 2.5 | 91.6 | 2.8 | 83.0 |
| | | 5 | 91.7 | 3.3 | 82.6 |
| | | 10 | 91.1 | 3.5 | 82.2 |
| TMCHT 3 | 50.9 | 2.5 | 91.8 | 2.8 | 83.1 |
| | | 5 | 91.2 | 3.1 | 83.3 |
| | | 10 | 91.2 | 3.4 | 82.4 |
| N-Et Q CHT (1:2) | 51.7 | 2.5 | 91.9 | 2.8 | 83.1 |
| | | 5 | 91.5 | 3.3 | 82.4 |
| | | 10 | 91.9 | 2.8 | 83.1 |
| N-Bu Q CHT (1:2) | 47.5 | 2.5 | 92.2 | 2.6 | 83.3 |
| | | 5 | 92.0 | 2.6 | 83.0 |
| | | 10 | 91.8 | 2.8 | 83.0 |
| N-Dod Q CHT (1:4) | 45.1 | 2.5 | 91.3 | 3.3 | 82.4 |
| | | 5 | 91.6 | 3.3 | 82.4 |
| | | 10 | 91.8 | 3.3 | 82.6 |
| N-Bz Q CHT (1:4) | 41.4 | 2.5 | 92.3 | 2.6 | 83.1 |
| | | 5 | 92.1 | 2.6 | 82.7 |
| | | 10 | 92.0 | 2.9 | 82.7 |
| N-Np Q CHT (1:4) | 40.0 | 2.5 | 92.2 | 2.7 | 83.3 |
| | | 5 | 91.8 | 3.3 | 82.6 |
| | | 10 | 91.1 | 3.3 | 82.1 |




Control
CHT treated
TMCHT1 treated
TMCHT2 treated
TMCHT3 treated
*N* – Alky/Aryl CHT treated
*N*-Alky/Aryl Q CHT treated

*DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40; WI: 10 deg/D65/Hunterlab*

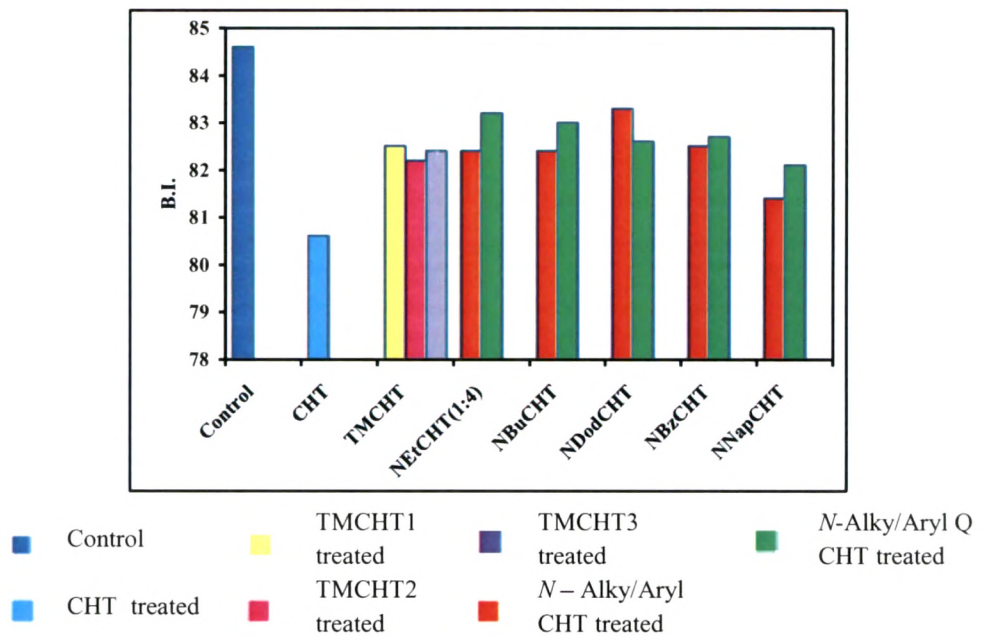
**Figure 4.26** Effect of *N*-Sub CHT treatment on whiteness of cotton fabric




Control
CHT treated
TMCHT1 treated
TMCHT2 treated
TMCHT3 treated
*N* – Alky/Aryl CHT treated
*N*-Alky/Aryl Q CHT treated

*DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40; YI: 2 deg/C/ASTM D 1925*

**Figure 4.27** Effect of *N*-Sub CHT treatment on yellowness of cotton fabric




*DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40; BI: 2 deg/C/TAPPI 452/ISO 2470*

**Figure 4.28** Effect of *N*-Sub CHT treatment on brightness of cotton fabric

It was observed from Table 4.26 and Table 4.27 that the appearance of the *N*-substituted CHT and their quaternized derivatives were satisfactory. With increase in concentrations of these derivatives, the appearance was very slightly affected and the differences were nominal. Figures 4.26, 4.27 & 4.28 revealed that the indices were decreased sharply due to CHT treatment and then improved due to N-substitution and then further improved by quaternization.

### *4.3.3.2 Effect of N- substituted CHT treatment on stiffness of cotton fabric*

Besides appearance, the appeal of cotton fabric is characterized by another inherent quality i.e. handle or feel which is popularly known as 'cotton-feel'. Treatment of CHT on cotton fabric, as illustrated in chapter 2, was found to impart undesired stiffness and impaired its handle. In order to sustain the inherent natural feel, the fabric was treated with *N*- alkyl and *N*-aryl CHT and their quaternized derivatives. The effect of chain length of *N*-alkyl substituent and the molecular size of *N*-aryl substituents on CHT

on the performance of cotton in context to handle is presented in Table 4.28. Very slight increase in stiffness was noticed due to the treatment of *N*-alkyl and *N*-aryl chitosan as against the parent chitosan treated fabrics. With increase in chain length of alkyl substituent the stiffness was gradually decreased indicating the improvement in handle. Almost similar trend was noticed in case of *N*-aryl substituted CHT derivatives. Quaternization of these *N*- substituted CHT derivatives, however, resulted into a slight introduction of stiffness. In case of TMCHT derivatives, the bending length was minimum at lower DQ and increased progressively with increase in DQ, nevertheless to a very small extent.

**Table 4.28** Effect of *N*- sub CHT treatment on stiffness of cotton fabric

| **Bending Length, cm** | | | | | | | |
|---|---|---|---|---|---|---|---|
| ***N*-Alkyl/Aryl CHT treated fabric** | | | | ***N*-Alkyl/Aryl Q CHT treated fabric** | | | |
| **Sample** | **DS, %** | **Warp** | **Weft** | **Sample** | **DQ, %** | **Warp** | **Weft** |
| Control | - | 2.05 | 1.68 | Control | - | 2.05 | 1.68 |
| CHT | - | 3.70 | 2.74 | CHT | - | 3.70 | 2.74 |
| TMCHT1 | - | - | - | TMCHT1 | 13.4 | 2.21 | 1.60 |
| TMCHT2 | - | - | - | TMCHT2 | 22.0 | 2.32 | 1.70 |
| TMCHT3 | - | - | - | TMCHT3 | 50.9 | 2.49 | 1.85 |
| N-Et CHT (1:2) | 45.5 | 2.46 | 1.70 | N-Et Q CHT (1:2) | 51.7 | 2.50 | 1.73 |
| N-Bu CHT (1:2) | 40.1 | 2.48 | 1.72 | N-Bu Q CHT (1:2) | 47.5 | 2.42 | 1.86 |
| N-Dod CHT (1:4) | 37.6 | 2.36 | 1.68 | N-Dod Q CHT (1:4) | 45.1 | 2.54 | 1.76 |
| N-Bz CHT (1:4) | 45.0 | 2.32 | 1.62 | N-Bz Q CHT (1:4) | 41.4 | 2.52 | 1.76 |
| N-Np CHT (1:4) | 37.6 | 2.38 | 1.60 | N-Np Q CHT (1:4) | 40.0 | 2.32 | 1.60 |

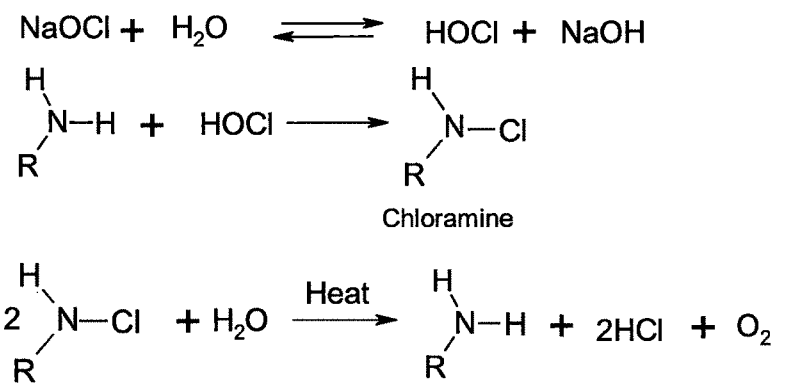
*Conc of CHT derivatives in pad liquor 10g/L*

The reduction in stiffness may be ascribed to the lubricating action of long chain hydrocarbon of alkyl group [2, 73] and also to the depolymerization of main CHT chain during *N*- substitution and quaternization processes as observed from the fall in intrinsic viscosity as discussed elaborately in proceeding chapter (Chapter 5). The feel of the fabric, evaluated by finger inspection, was very satisfactory. The fabric smoothness was

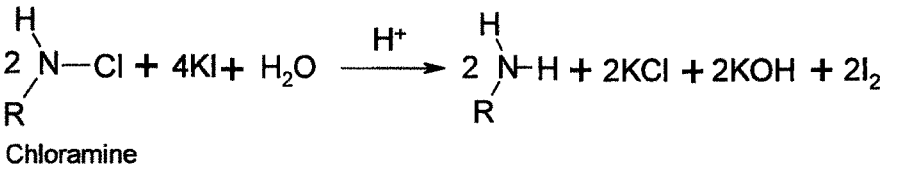
improved with increase in molecular size of *N*-substituents. This may again attributed to the softness effect of hydrocarbon side groups.

### *4.3.3.3 Effect of N-substituted CHT treatment on chlorine retention property*

The appearance of cotton fabric treated with compounds containing free -NH- groups such as aminoplasts, cationic softeners, amino silicones etc is severely affected due to yellowness caused by chlorine retention. This property also of free -NH- group containing compounds leads to tremendous loss in fibre strength, produces rancid/bad odour and is toxic due to the formation of chloramines as shown in scheme 4.13. Since chitosan belongs to polycation containing pendant amino groups which are sites for chlorine retention. The object of *N*- modification, in part, in present work was to reduce the chlorine retention problem. The process of yellowing, however, was a very slow. In order to intensify the yellowness for faster evaluation, the samples were treated with solution containing potassium iodide and acetic acid where in the formed chloarmie reacts with acidic potassium iodide to liberate iodine as shown in scheme 4.14 [1]. Effect of quaternization of *N*- substituted CHT on appearance and tensile strength of cotton fabric due to chlorine retention is illustrated in Table 4.29 and graphically in Figure 4.29 and Figure 4.30.




**Scheme 4.13** Reactions involved in chlorine retention




**Scheme 4.14** Reaction of chloramine with potassium iodide

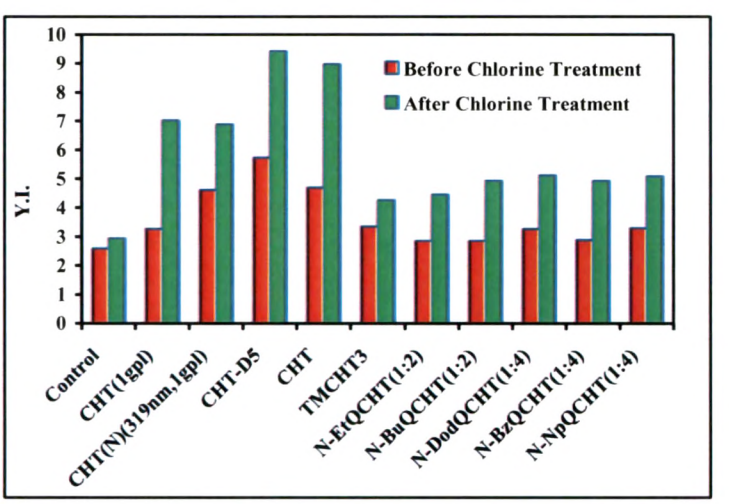
**Table 4.29** Effect of different CHT and *N*- sub CHT derivatives treatment on chlorine retention on cotton fabric

| Sample | Conc in pad bath, g/L | YI | | Tenacity, g/tex | | |
|---|---|---|---|---|---|---|
| | | Before chlorine treatment | After chlorine treatment | Before chlorine treatment | After chlorine treatment | Loss in strength (%) |
| Untreated cotton | - | - | - | 23.33 | 21.18 | 9.22 |
| Control | - | 2.6 | 2.9 | 20.87 | 18.63 | 10.73 |
| CHT | 1 | 3.3 | 7.0 | 20.48 | 17.48 | 14.63 |
| CHT(N) | 1 | 4.6 | 6.9 | 25.61 | 20.81 | 18.74 |
| CHT-D5 | 10 | 5.7 | 9.4 | 22.08 | 16.74 | 24.18 |
| CHT | 10 | 4.7 | 9.0 | 21.77 | 15.64 | 28.16 |
| TMCHT3 | 10 | 3.4 | 4.3 | 21.18 | 19.71 | 6.94 |
| N-Et Q CHT(1:2) | 10 | 2.9 | 4.5 | 21.68 | 20.16 | 7.01 |
| N-Bu Q CHT(1:2) | 10 | 2.9 | 4.9 | 20.14 | 18.77 | 6.87 |
| N-Dod Q CHT(1:4) | 10 | 3.3 | 5.1 | 21.36 | 19.69 | 7.81 |
| N-Bz Q CHT(1:4) | 10 | 2.9 | 4.9 | 21.81 | 20.05 | 8.05 |
| N-Np Q CHT(1:4) | 10 | 3.3 | 5.1 | 19.92 | 18.33 | 7.96 |

*CHT (N): Particle size 319.4nm, Mol wt: CHT-D5 =11986, CHT= 135,839, DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40*

The results shown in Table 4.29 and in Figures 4.29 & 4.30 clearly revealed that the cotton fabric treated with different grades of CHT without *N*-modification was susceptible to chlorine damage. With increase in concentration of CHT, the yellowness problem and tensile strength losses were found to be increased. The change in molecular

weight of chitosan showed some anomaly. The appearance of CHT-D5 (low mol wt chitosan) was poorer than the CHT (high mol wt chitosan). This may be attributed to the yellowness imparted to CHTD 5 during depolymerization process itself as observed from Y.I. of CHTD5 before chlorine treatment in the Figures 4.29. The reduction in particle size e.g. CHT (N) showed greater susceptibility to chlorine damage than the normal CHT. This was expected, because smaller particle sizes have greater reactivity and also penetrate more in to the fibre structure leading to more proximity of fibre for such degradation reactions. The *N*-substitution and quaternization of CHT were found to overcome the chlorine retention problem substantially. The yellowness imparted and the fibre strength losses were nominal. No definite trend was observed in context to the chain length or molecular size of substituents. However, trimethyl chitosan derivative was found to be somewhat more resistant to chlorine damage than the *N*-alkyl or *N*-aryl quaternized CHT derivatives.




*Conc in pad bath 10 g/L, CHT (N): Particle size 319.4nm, Mol wt: CHT-D5 =11986, CHT= 135,839, DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40*

**Figure 4.29** Effect of *N*-Sub CHT treatment on yellowness of cotton fabric due to chlorine retention

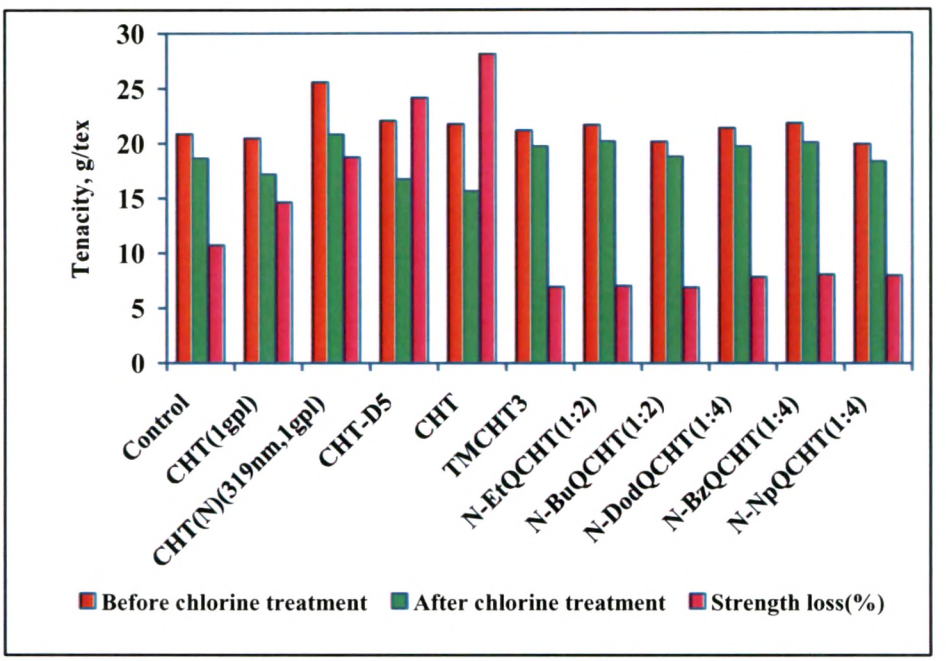



**Figure 4.30** Effect of *N*-Sub CHT treatment on fibre strength of cotton due to chlorine retention

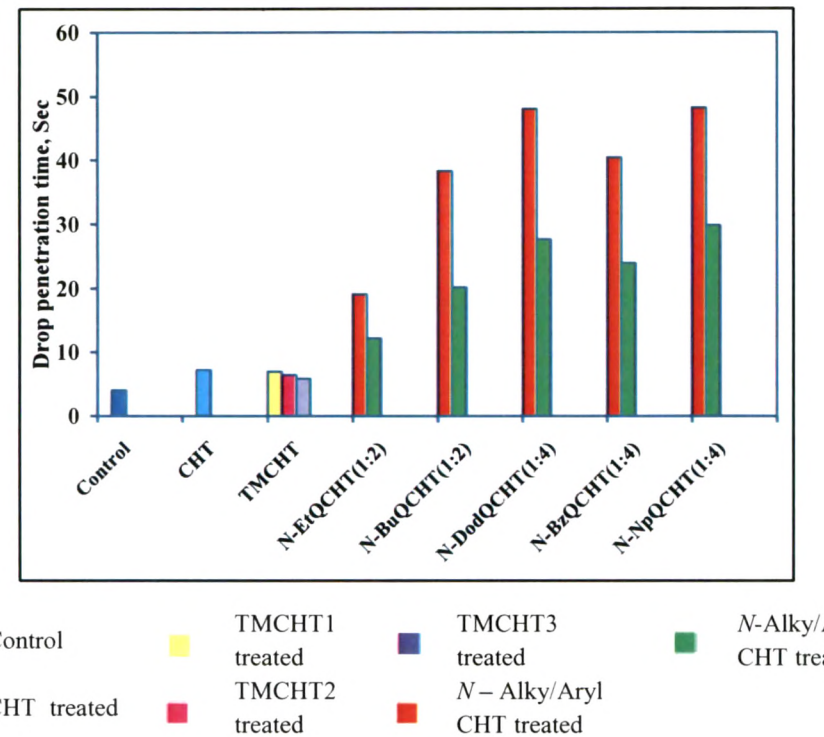
### *4.3.3.4 Effect of N- substituted CHT treatment on absorbency of cotton fabric*

The absorbency of *N*-alkyl and *N*-aryl CHT and their quaternized derivatives treated cotton fabric were measured by drop penetration method. The results are presented in Table 4.30 and graphically in Figure 4.31.

**Table 4.30** Effect of *N*-sub CHT treatment on absorbency of cotton fabric

| ***N*-Alkyl/Aryl CHT treated fabric** | | | ***N*-Alkyl/Aryl Q CHT treated fabric** | | |
|---|---|---|---|---|---|
| **Sample** | **DS, %** | **Absorbency, Sec** | **Sample** | **DQ, %** | **Absorbency, Sec** |
| Control | - | 4.0 | Control | - | 4.0 |
| CHT | - | 7.2 | CHT | - | 7.2 |
| TMCHT1 | - | - | TMCHT1 | 13.4 | 7.0 |
| TMCHT2 | - | - | TMCHT2 | 22.0 | 6.4 |
| TMCHT3 | - | - | TMCHT3 | 50.9 | 5.8 |
| N-Et CHT (1:2) | 45.5 | 19.1 | N-Et QCHT (1:2) | 51.7 | 12.2 |
| N-Bu CHT (1:2) | 40.1 | 38.3 | N-Bu Q CHT (1:2) | 47.5 | 20.2 |
| N-Dod CHT (1:4) | 37.6 | 48.1 | N-Dod QCHT(1:4) | 45.1 | 27.7 |
| N-Bz CHT (1:4) | 45.0 | 40.5 | N-Bz QCHT(1:4) | 41.4 | 24.0 |
| N-Np CHT (1:4) | 37.6 | 48.3 | N-Np QCHT(1:4) | 40.0 | 29.8 |

*Conc of CHT derivatives in pad liquor 10g/L*




*DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40*

**Figure 4.31** Effect of *N*-sub CHT treatment on absorbency of cotton fabric

The absorbency was affected due to alkyl or aryl substituents and was decreased with increase in molecular size of substituents. Quaternization of CHT and *N*-Sub CHT derivatives was found to improve the absorbency of treated fabric substantially. In case of TMCHT, the absorbency was increased progressively with increase in DQ. The hydrophobicity imparted by *N*-alkyl or aryl groups was overcome by the quaternization yet the effect due to hydrophobic substituents did persist. Quaternization results the amino groups in to quaternary ammonium salts which are permanently in ionic form. These cat ions can easily get surrounded by water molecules due to ion-dipole forces [22, 74] and thus increase the absorbency.

#### *4.3.5.5 Effect of N- substituted CHT treatment on direct dyeing of cotton fabric*

A significant improvement in dye uptake due chitosan treatment of cotton fabric has been revealed in 2.3.13.1, chapter 2. The pendant amino groups of chitosan, however,

are not completely in ionic form in neutral or alkaline bath. The cationic charge on chitosan can only be developed when protonated, as in acidic medium. Cotton dyeing, however, conventionally is carried out in alkaline dye baths and therefore complete exhaustion of such dyes on chitosan treated fabric is not achieved. In view of this, a permanent cationic charge with improved hydrophilicity on the chitosan macromolecule was developed by quaternization protocol.

**Table 4.31A** Effect of *N*-sub CHT treatment on direct dyeing of cotton fabric

| **Sample** | **Conc in pad liquor, g/L** | **K/S values** | | | |
|---|---|---|---|---|---|
| | | **C. I. Direct Red 81** | | **C. I. Direct Blue 71** | |
| | | **Conventional dye bath** | **Salt free dye bath** | **Conventional dye bath** | **Salt free dye bath** |
| Control | - | 7.73 | 5.86 | 7.41 | 5.48 |
| CHT | 2.5 | 9.41 *[22]* | | 9.60 *[29]* | |
| | 5 | 10.16 *[32]* | | 10.81 *[46]* | |
| | 10 | 10.97 *[42]* | 9.89 | 12.42 *[68]* | 10.78 |
| TMCHT1 | 2.5 | 9.94 *[29]* | | 9.94 *[34]* | |
| | 5 | 10.86 *[41]* | | 11.58 *[56]* | |
| | 10 | 11.39 *[48]* | 10.37 | 12.06 *[63]* | 10.86 |
| TMCHT2 | 2.5 | 10.63 *[38]* | | 10.14 *[37]* | |
| | 5 | 11.39 *[48]* | | 11.69 *[58]* | |
| | 10 | 12.01 *[56]* | 11.29 | 12.28 *[66]* | 11.42 |
| TMCHT3 | 2.5 | 11.47 *[49]* | | 10.58 *[43]* | |
| | 5 | 11.86 *[54]* | | 11.91 *[61]* | |
| | 10 | 12.40 *[61]* | 11.90 | 12.73 *[72]* | 11.97 |

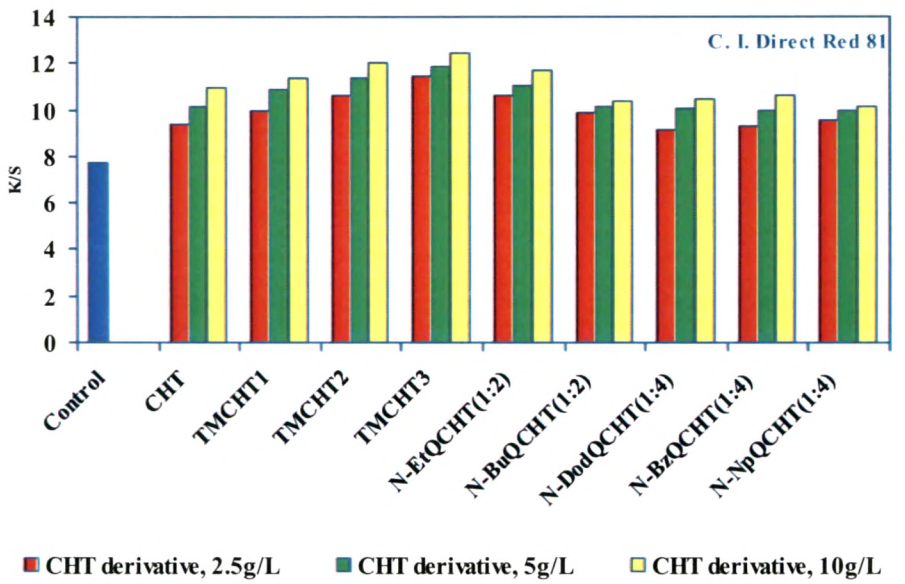
*Dye 1% o.w.m, Values in brackets indicate the change in colour value from control*

**Table 4.31B** Effect of *N*-sub CHT treatment on direct dyeing of cotton fabric

| Sample | Conc in pad liquor, g/L | K/S values | | | |
|---|---|---|---|---|---|
| | | C. I. Direct Red 81 | | C. I. Direct Blue 71 | |
| | | Conventional dye bath | Salt free dye bath | Conventional dye bath | Salt free dye bath |
| Control | - | 7.73 | 5.86 | 7.41 | 5.48 |
| N-Et QCHT (1:2) | 2.5 | 10.66 *[38]* | | 10.43 *[41]* | |
| | 5 | 11.01 *[43]* | | 11.84 *[60]* | |
| | 10 | 11.70 *[52]* | 10.89 | 12.36 *[67]* | 11.37 |
| N-Bu QCHT (1:2) | 2.5 | 9.86 *[28]* | | 10.36 *[40]* | |
| | 5 | 10.09 *[31]* | | 10.95 *[48]* | |
| | 10 | 10.39 *[35]* | 10.08 | 11.03 *[49]* | 10.19 |
| N-Dod Q CHT (1:4) | 2.5 | 9.16 *[19]* | | 10.06 *[36]* | |
| | 5 | 10.01 *[30]* | | 10.51 *[42]* | |
| | 10 | 10.47 *[36]* | 10.16 | 10.43 *[41]* | 9.60 |
| N-Bz QCHT (1:4) | 2.5 | 9.32 *[21]* | | 9.77 *[32]* | |
| | 5 | 9.93 *[29]* | | 10.21 *[38]* | |
| | 10 | 10.63 *[38]* | 10.31 | 10.51 *[42]* | 9.72 |
| N-Np QCHT (1:4) | 2.5 | 9.55 *[24]* | | 9.77 *[32]* | |
| | 5 | 9.94 *[29]* | | 9.92 *[34]* | |
| | 10 | 10.16 *[32]* | 9.86 | 10.21 *[38]* | 9.45 |

*Dye: 1% o.w.m., Values in brackets indicate the change in colour value from control, DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40*

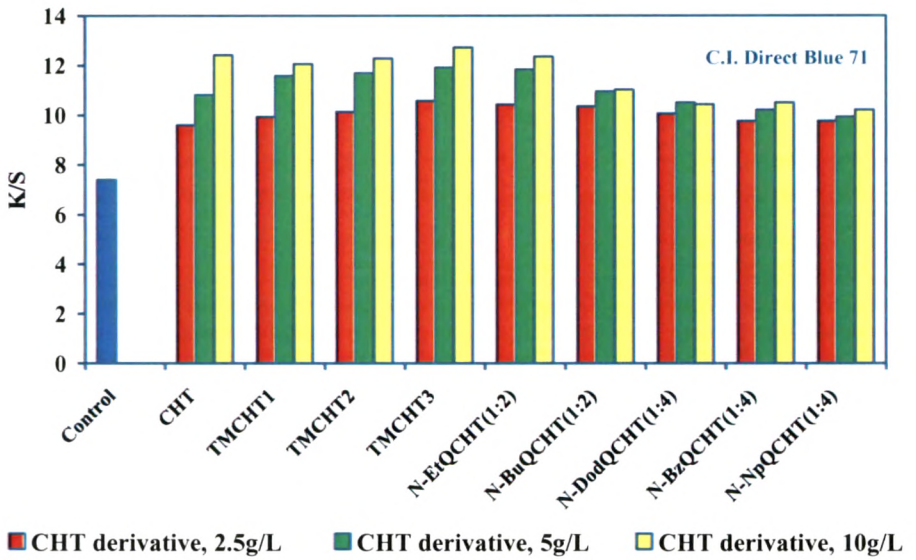
Thus the effect of quaternized *N*- alkyl and *N*-aryl CHT derivatives on dyeing behaviour of cotton fabric was studied. The effects of different *N*- modified chitosans treatment on direct dyeing of cotton fabric, measured in terms of K/S, are shown in Table 4.31(A&B) and graphically in the Figures 4.32 and 4.33 respectively; and their washing fastnesses are presented in Table 4.32.




*Dye (C. I. Direct Red 81)1% o.w.m, DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40*

**Figure 4.32** Effect of *N*-sub CHT treatment on direct dyeing of cotton fabric

It was observed from Table 4.31(A & B) and corresponding Figure 4.32 and Figure 4.33 that the dye uptake on cotton fabric for both the dyes increased with increase in concentration of each CHT derivative treatment. The degree of quaternization also influenced the dyeability of treated fabric. The dyeability was increased progressively with DQ for TMCHT. However, for a given degree of substitution, the dye uptake was declined with increase in alkyl chain length and aryl groups. As the quaternization imparts permanent cations on CHT can establish ionic linkages with anionic groups on direct dyes. Thus the synergistic effect of ionic linkages between quaternized CHT and dye together with usual dye- fibre and Dye-TMCHT bonds such as H-bonds and other physical forces showed the enhanced dye uptake for quaternized CHT derivative treated fabrics.



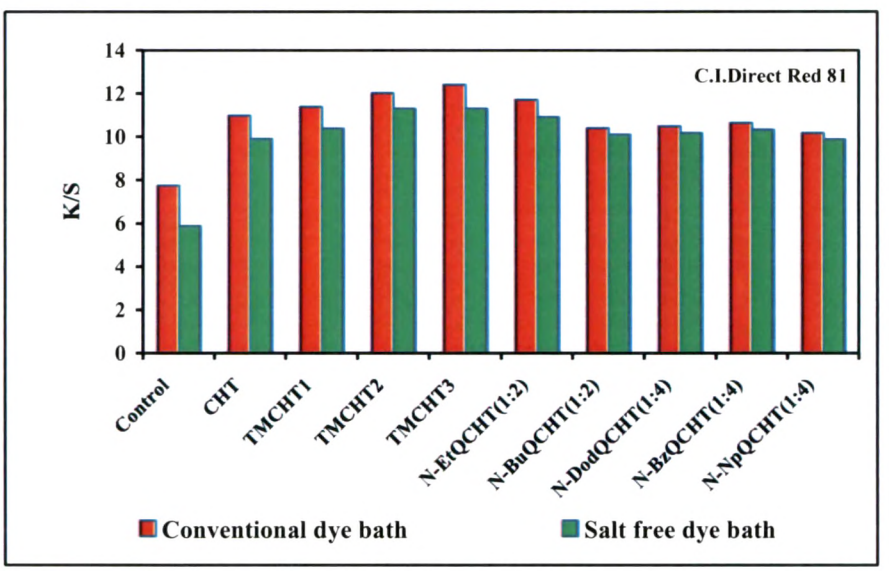

*Dye (C. I. Direct Blue 71)1% o.w.m, DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40*

**Figure 4.33** Effect of *N*-sub CHT treatment on direct dyeing of cotton fabric

With increase in chain length of *N*- alkyl substituent by methylene spacer and molecular size of *N*-aryl substituent by benzene rings, hydrophobic barrier between the dye and the fibre is created due to the bulkier side groups showing declined trend of dye uptake. The effect of hydrophobicity was more prominently seen with *N*- Dod Q CHT and *N*-Np Q CHT derivatives treated fabrics. The higher hydrophobicity due to these derivatives treatment has also been verified from absorbency data from Table 4.30 or Figure 4.31. The decreased dyeability due to hydrophobic substituents was overcome with quaternization of the *N*- substituted CHT derivatives. Thus for lower *N*- substituted CHT derivatives the dyeing was governed by degree of quaternization showing enhanced dye uptake while for higher derivatives the dyeing was governed by two diverse phenomena namely, one decreased dyeability due to bulkier substituents and second the increased dyeability due to quaternary groups.

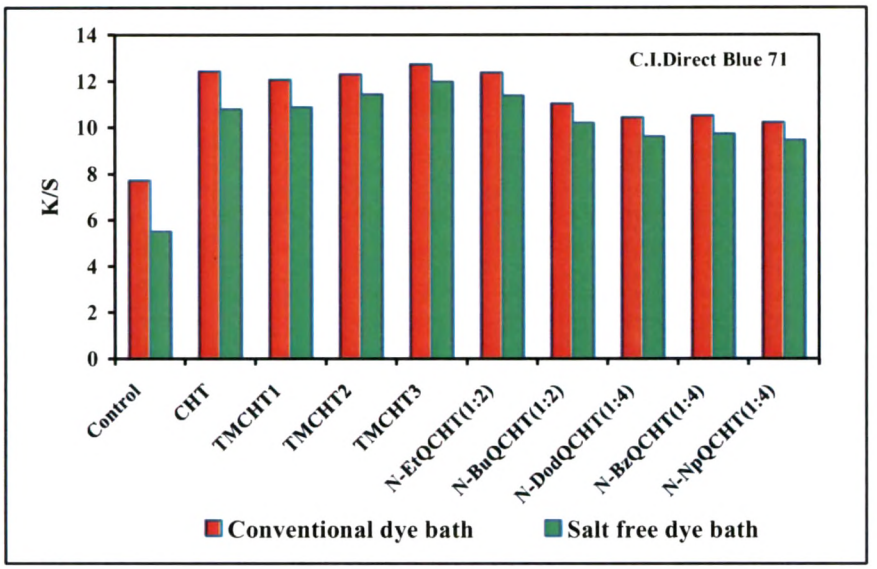
In order to understand the attributes of cations of quaternary ammonium groups for enhanced dyeability, we compared the dyeing results of salt free dye bath with that of conventional dye bath as illustrated in Table 4.31 (A&B) and in Figures 4.34, 4.35 and

4.36. It was found that the difference in dye uptake (colour difference) between conventional and salt free dye bath samples was sharply dropped due to quaternization i.e. diminishing the role of electrolyte in dye bath in case of quaternized CHT treated fabrics. Thus, according the theory of cotton dyeing [75] the fibre acquires -ve zeta potential that is responsible for repulsion of anionic direct dyes. The added salt in dye bath dissipates the -ve charge due the adsorption of inorganic +ve ions facilitating the adsorption of direct dyes on fibre by virtue of its affinity. This phenomenon of charge dissipation is now performed by cat ions of quaternized CHT derivatives. Thus these cations serve two purposes i.e. the -ve charge dissipation on fibre surface and the formation of salt linkages with dye.



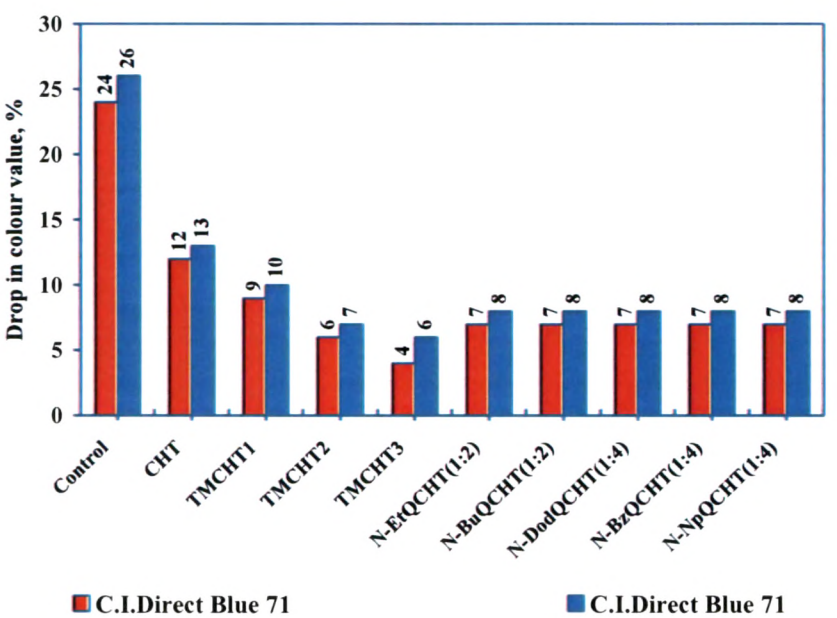

*N-Alkyl/Aryl Q CHT in pad liquor 10 g/L, Dye (C. I. Direct Red 81) 1% o.w.m, DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40*

**Figure 4.34** Effect of dye bath condition on direct dyeing of *N*-Sub CHT treated cotton fabric




*N- Alkyl/Aryl Q CHT in pad liquor 10 g/L, Dye (C. I. Direct Red 81) 1% o.w.m, DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40*

**Figure 4.35** Effect of dye bath condition on direct dyeing of *N*-Sub CHT treated cotton fabric




*N- Alkyl/Aryl Q CHT in pad liquor 10 g/L, Dye 1% o.w.m*

**Figure 4.36** Drop in colour value of salt free dyeing from conventional dye bath in direct dyeing of *N*-Sub Q CHT treatment of cotton fabric

The influence of quaternization of CHT and *N*-substituted CHT on washing fastness of direct dyes is enumerated in Table 4.32. It was observed that the fastness was slightly improved with increase in DQ of TMCHT treated samples but was again affected due to *N*- alkyl chain length or *N*-aryl groups. The attachment of dye molecules to quaternary ammonium groups on TMCHT is comparatively stronger due to their ionic interaction and therefore is firmly retained by the TMCHT treated fibres. The hydrophobic large side groups due to *N*- substitution weaken the attachments between dye and quaternary groups due to pushing of dye away from the sites resulting into poor fastness. The overall fastness washing, however, is determined by the simultaneous effects of attachment of dye with the dye sites on fibre and CHT derivatives and the interaction between the CHT derivative sand the fibre.

**Table 4.32** Effect of *N*-sub CHT treatment on washing fastness of direct dyed cotton fabrics

| Sample | Conc in pad bath, g/L | Washing fastness ratings | | | |
|---|---|---|---|---|---|
| | | C. I. Direct Red 81 | | C. I. Direct Blue 71 | |
| | | Change in Color | Staining | Change in Color | Staining |
| Control | - | 3 | 3 | 4-5 | 3-4 |
| CHT | 5 | 3 | 2-3 | 4-5 | 3-4 |
| | 10 | 3-4 | 2-3 | 4-5 | 3-4 |
| TMCHT1 | 5 | 3-4 | 3 | 4-5 | 3-4 |
| | 10 | 3-4 | 3 | 4-5 | 3-4 |
| TMCHT2 | 5 | 3-4 | 3-4 | 4-5 | 3-4 |
| | 10 | 3-4 | 3-4 | 4-5 | 3-4 |
| TMCHT3 | 5 | 4 | 3-4 | 4-5 | 4 |
| | 10 | 4-5 | 3-4 | 4-5 | 4 |
| N-Et QCHT (1:2) | 5 | 3-4 | 3 | 4-5 | 4 |
| | 10 | 3-4 | 3 | 4-5 | 4 |
| N-Bu QCHT (1:2) | 5 | 3 | 2-3 | 3-4 | 3-4 |
| | 10 | 2-3 | 2-3 | 3-4 | 3-4 |
| N-Dod QCHT (1:4) | 5 | 2 | 2-3 | 3 | 3-4 |
| | 10 | 2 | 2 | 3 | 3-4 |
| N-Bz QCHT (1:4) | 5 | 2-3 | 2-3 | 3-4 | 3-4 |
| | 10 | 2-3 | 2-3 | 3-4 | 3-4 |
| N-Np QCHT (1:4) | 5 | 2-3 | 2-3 | 3-4 | 3-4 |
| | 10 | 2-3 | 2-3 | 3-4 | 3 |

#### 4.3.3.6 *Effect of N- substituted chitosan treatment on colour depth of direct dyed cotton fabric*

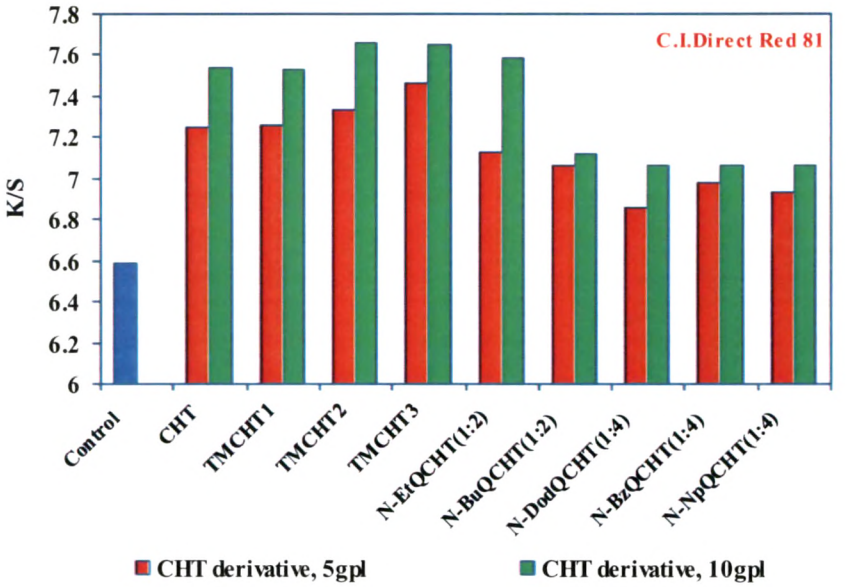
It was observed from previous discussion that the *N*-substitution of CHT treatment improved the handle of the fabric substantially. It is also anticipated that such modifications play important role in on other properties of treated fabrics such as wrinkle recovery, antibacterial and soil release and hence these products can be employed as a textile finishing auxiliary. Treatment of *N*- modified chitosan, like parent chitosan as discussed in chapter 2, can alter the colour value and fastness properties of dyed fabrics. The effect of post dyeing treatment of different *N*- substituted CHT derivatives direct dyed cotton fabric are presented in Table 4.33 and Table 4.34 and graphically in Figures 4.37 and 4.38. It was observed that the two dyes respond differently for the CHT derivative treatments. The C.I. Direct Red 81dyed fabrics showed improved intensity of colour than that of C.I. Direct Blue 71dyed samples. The colour depth of both the shades was found to be increased with increase in concentration of CHT derivatives treatments. The maximum intensity, in both the dyes, was observed when the dyed fabrics were treated with TMCHT3. It means higher the degree of quaternization; the more will be the shade darker. The apparent changes in shade may be attributed to the migration of dye from fibre phase to CHT derivatives phase. The quaternary ammonium sites being permanently cat ionic and responsible for hydrophilicity, can readily interact with anions ($-SO_3^-$ groups) of dye. As the molecular size of substituent is increased the probability of such interactions is lowered and hence the extent of migration of dye towards CHT derivative layer is lowered. Further, the easily washable C.I. Direct Red 81dye is migrated to greater extent from fabric to CHT derivative layer during pad application and then drying. The washing fastness of post dyeing CHT derivative treatment was found to be slightly improved. This may be attributed to the complex formation between dye and the CHT derivatives through salt linkages.

**Table 4.33** Effect of *N*-Sub CHT treatment on colour depth of direct dyed cotton fabrics (Post dyeing treatment)

| Sample | Conc in pad liquor, g/L | C.I. Direct Red 81 | | C.I. Direct Blue 71 | |
|---|---|---|---|---|---|
| | | K/S value | *Colour change, % | K/S value | *Colour change, % |
| Control (Dyed) | - | 6.59 | - | 7.29 | - |
| CHT | 5 | 7.25 | 9 | 6.83 | -7 |
| | 10 | 7.54 | 14 | 7.31 | 3 |
| TMCHT1 | 5 | 7.26 | 10 | 6.94 | -5 |
| | 10 | 7.53 | 14 | 7.52 | 3 |
| TMCHT2 | 5 | 7.33 | 11 | 7.37 | 1 |
| | 10 | 7.66 | 16 | 7.52 | 3 |
| TMCHT3 | 5 | 7.46 | 13 | 7.61 | 3 |
| | 10 | 7.65 | 16 | 7.67 | 5 |
| N-Et QCHT (1:2) | 5 | 7.13 | 8 | 7.45 | 2 |
| | 10 | 7.59 | 15 | 7.74 | 6 |
| N-Bu QCHT (1:2) | 5 | 7.06 | 7 | 7.40 | 1 |
| | 10 | 7.12 | 8 | 7.53 | 3 |
| N-Dod QCHT (1:4) | 5 | 6.86 | 4 | 7.23 | -1 |
| | 10 | 7.06 | 7 | 7.45 | 2 |
| N-Bz QCHT (1:4) | 5 | 6.98 | 6 | 7.15 | -2 |
| | 10 | 7.06 | 7 | 7.38 | 1 |
| N-Np QCHT (1:4) | 5 | 6.93 | 5 | 7.16 | -2 |
| | 10 | 7.06 | 7 | 7.30 | -- |

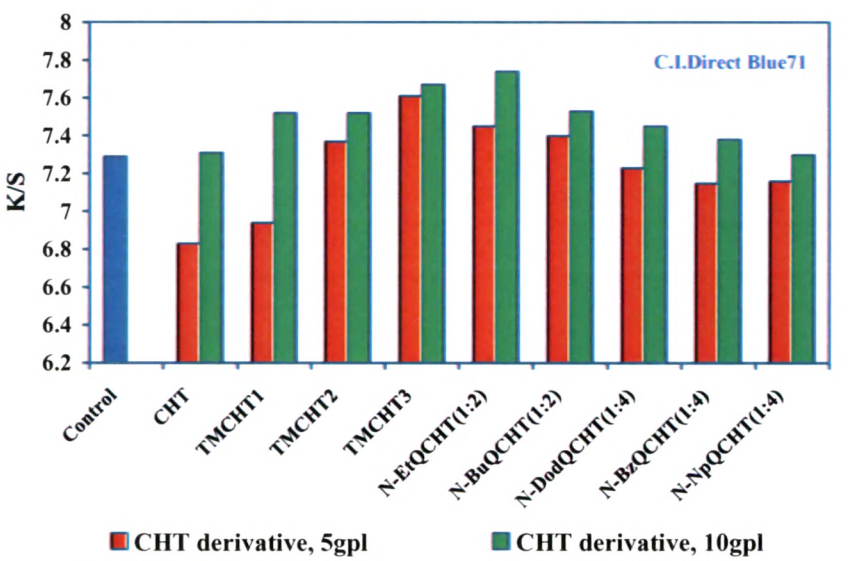
*Dye 1% o.w.m, DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40*

**Colour change from dyed control sample*




*Dye (C. I. Direct Red 81) 1% o.w.m, DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40*

**Figure 4.37** Effect of *N*-Sub CHT treatment on colour depth of direct dyed cotton fabrics




*Dye (C. I. Direct Blue 71) 1% o.w.m, DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40*

**Figure 4.38** Effect of *N*-Sub Q CHT derivatives treatment on colour depth of direct dyed cotton fabrics

**Table 4.34** Effect of *N*-sub CHT treatment on washing fastness of direct dyed cotton fabric

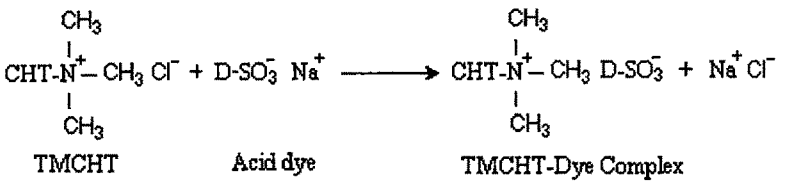
| Sample | Washing Fastness | | | |
|---|---|---|---|---|
| | CI Direct Red 81 | | CI Direct Blue 71 | |
| | Change in Colour | Staining | Change in Colour | Staining |
| Control (Dyed) | 3 | 3 | 4-5 | 3 |
| CHT | 3-4 | 2-3 | 4 | 4-5 |
| TMCHT1 | 3-4 | 2-3 | 4 | 4 |
| TMCHT2 | 3-4 | 3 | 4-5 | 4 |
| TMCHT3 | 4-5 | 3-4 | 4-5 | 4-5 |
| N-Et QCHT (1:2) | 3 | 3 | 4 | 4 |
| N-Bu QCHT (1:2) | 3-4 | 3 | 4 | 4-5 |
| N-Dod QCHT (1:4) | 3-4 | 3 | 4-5 | 4 |
| N-Bz QCHT (1:4) | 3-4 | 3 | 4-5 | 4-5 |
| N-Np QCHT (1:4) | 3-4 | 3 | 4-5 | 4 |

*Dye: 1% o.w.m, Conc of CHT derivatives in pad bath 10 g/L, DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40*

### *4.3.3.7 Effect of N- substituted CHT treatment on acid dyeing*

Attributing to cationic nature of CHT derivatives, the work was extended to investigate the effect on dyeability of CHT derivatives treated cotton fabric towards acid dye, which is non dyeable towards normal cotton. The results are presented in Table 4.35 and in Figure 4.39. It was revealed from these demonstrations that the CHT and quaternized CHT derivatives treated cotton fabrics dyed substantially with C.I. Acid Blue158 as against only a tint on control. Since quaternary ammonium site of TMCHT and quaternized *N*-Sub CHT should form ionic linkages with stoichiometric amount of anionic acid dyes as illustrated by the scheme 4.15 in neutral dye bath. The CHT derivatives treated fabric in acidic dye bath showed almost similar extent of exhaustion of acid dye except little decline in higher derivatives. In acidic medium, besides quaternary ammonium sites, almost all remaining amino groups are believed to get protonated and therefore a similar dye uptake was observed as expected. Little decrease in dye uptake in higher CHT derivative treated fabric may be due to the steric hindrance of bulkier side groups. In neutral dye bath, the dyeing phenomenon follows the ion exchange reaction of

scheme 4.15.Therefore a progressive increase in dye uptake corresponding to degree of quaternization (stoichiometry) was observed.

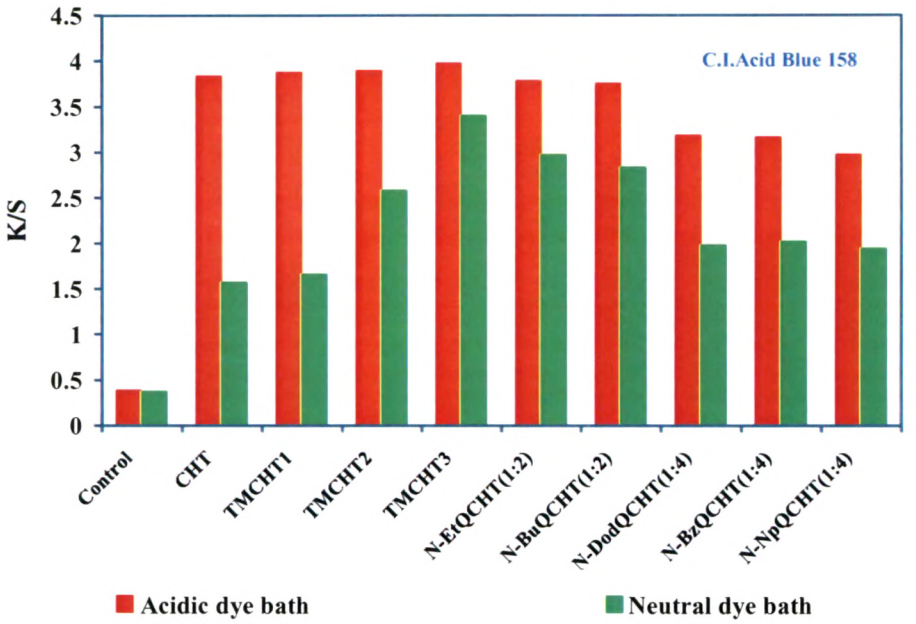



**Scheme 4.15** Reaction trimethyl chitosan ammonium chloride salt with acid dye

**Table 4.35** Effect of *N*-Sub CHT treatment on dyeing with C.I. Acid Blue158

| Sample | Conc in pad bath, g/L | K/S Value | |
|---|---|---|---|
| | | Acidic Dye bath | Neutral Dye bath |
| Control | - | 0.38 | 0.37 |
| CHT | 5 | 2.10 | 0.79 |
| | 10 | 3.83 | 1.57 |
| TMCHT1 | 5 | 2.15 | 1.06 |
| | 10 | 3.87 | 1.66 |
| TMCHT2 | 5 | 2.13 | 1.34 |
| | 10 | 3.89 | 2.58 |
| TMCHT3 | 5 | 2.19 | 1.76 |
| | 10 | 3.97 | 3.40 |
| N-Et QCHT (1:2) | 5 | 2.08 | 1.17 |
| | 10 | 3.78 | 2.97 |
| N-BuQCHT (1:2) | 5 | 2.07 | 1.07 |
| | 10 | 3.75 | 2.83 |
| N-Dod QCHT (1:4) | 5 | 2.05 | 0.91 |
| | 10 | 3.18 | 1.98 |
| N-Bz QCHT (1:4) | 5 | 1.99 | 0.97 |
| | 10 | 3.16 | 2.02 |
| N-Np QCHT (1:4) | 5 | 1.98 | 0.85 |
| | 10 | 2.97 | 1.94 |

*Dye: 2% o.w.m, DQ(%): TMCHT1=13.4,TMCHT2=22,TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40*




*Dye (C.I. Acid Blue158) 2% o.w.m, Conc in pad bath 10 g/L, DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40*

**Figure 4.39** Effect of *N*-Sub CHT treatment on dyeing with acid dye

### *4.3.3.8 Effect of N-substituted CHT treatment on wrinkle recovery properties of cotton fabric*

The chitosan treatment was found to impair the wrinkle recovery property of cotton fabric. The problem of creasing was attributed, mostly, to surface coating of non elastic stiff film that deform easily when pressed. Indeed, the wrinkle recovery property governed is mainly by the cross linking phenomenon that is not taking place with/by CHT treatment. In order to understand the influence of quaternization and *N*- substitution of CHT by varying length of alkyl chain and molecular size of aryl groups to the resiliency of cotton fabrics, the CRA of CHT derivative treated fabrics against commercial cross linking agents was evaluated. The performances of these treated samples are demonstrated in Table 4.36 and Table 4.37. It was observed from these tables that the resiliency improved nevertheless did not reach the commercial requirements of DMDHEU. Addition of commercial cross linking agents to the pad bath formulation is recommended.

**Table 4.36** Wrinkle recovery property of *N*-sub CHT treated cotton fabric

| Sample | CRA$^0$ of fabric treated at: | |
|---|---|---|
| | 5 g/L | 10 g/L |
| CHT | 140 | 125 |
| TMCHT1 | 171 | 167 |
| TMCHT2 | 172 | 175 |
| TMCHT3 | 177 | 174 |
| N-Et QCHT (1:2) | 169 | 167 |
| N-Bu QCHT (1:2) | 172 | 175 |
| N-Dod QCHT (1:4) | 175 | 176 |
| N-Bz QCHT (1:4) | 167 | 166 |
| N-Np QCHT (1:4) | 164 | 161 |

*CRA of Control: 161$^0$, DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9;*
*DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5,*
*N-Dod Q CHT (1:4) = 37.6/45.1, N-Bz Q CHT (1:4) = 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40*

**Table 4.37** Wrinkle recovery property of DMDHEU treated cotton fabric

| DMDHEU, g/L | CRA$^0$ |
|---|---|
| Control | 161 |
| 20 | 180 |
| 40 | 207 |
| 60 | 215 |
| 80 | 226 |
| 100 | 233 |

### *4.3.3.9 Effect of N- substituted CHT treatment on soiling behaviour of cotton fabric*

Besides creasing tendency, the appeal of garments is also severely hampered due to another phenomenon, namely soiling. It arises due deposition of different kinds of undesired impurities termed as 'soil' through various agencies such as contact transfer, medium transfer, electrostatic attraction etc as described in literature [73, 76-79]. Of the particular concern with the oily soil that is most commonly observed, the oil forms a thin film around individual fibre. This film leads to increased build-up with successive soilings and serves as adhesive for particulate matter, thus greatly affecting the cloth

appearance. The oily soil most often deposited on garments is human sebum which is a complex mixture of lipids.

**Table 3.38** Effect of different CHT and *N*- sub CHT treatment on soiling of cotton fabric

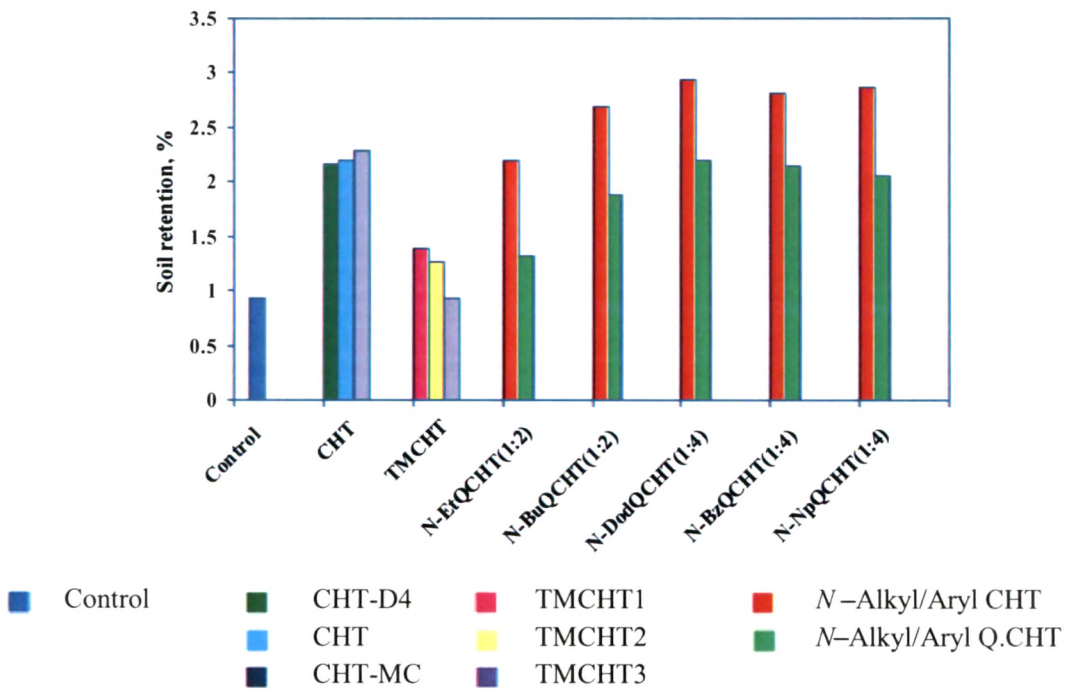
| Sample | *N*-Alkyl/Aryl CHT treated fabric | | | Sample | *N*-Alkyl/Aryl Q CHT treated fabric | | |
|---|---|---|---|---|---|---|---|
| | Initial wt (A), g | Wt after soaping (B), g | Soil retention, % $\frac{B-A}{A}\times 100$ | | Initial wt (A), g | Wt after soaping (B), g | Soil retention, % $\frac{B-A}{A}\times 100$ |
| Control | 1.2949 | 1.3071 | 0.94 | Control | 1.2949 | 1.3071 | 0.94 |
| CHT-D4 | 1.2653 | 1.2928 | 2.17 | TMCHT 1 | 1.2553 | 1.2738 | 1.39 |
| CHT | 1.2611 | 1.2888 | 2.20 | TMCHT 2 | 1.2388 | 1.2544 | 1.26 |
| CHT-MC | 1.3260 | 1.3562 | 2.28 | TMCHT 3 | 1.2637 | 1.2756 | 0.94 |
| N-Et CHT (1:2) | 1.2932 | 1.3217 | 2.20 | N-Et Q CHT(1:2) | 1.2680 | 1.2847 | 1.32 |
| N-Bu CHT (1:2) | 1.2688 | 1.3029 | 2.69 | N-Bu Q CHT (1:2) | 1.2813 | 1.3054 | 1.88 |
| N-Dod CHT (1:2) | 1.2731 | 1.3101 | 2.93 | N-Dod Q CHT(1:2) | 1.2771 | 1.3050 | 2.19 |
| N-Bz CHT (1:4) | 1.2589 | 1.2943 | 2.81 | N-Bz Q CHT (1:4) | 1.2689 | 1.2962 | 2.15 |
| N-Np CHT (1:4) | 1.2813 | 1.3179 | 2.86 | N-Np Q CHT (1:4) | 1.2800 | 1.3066 | 2.05 |

*Conc in pad bath 10 g/L, Mol wt: CHT-D4:20698, CHT: 135,839, CHT-MC: 654,127,*
*DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40*

Thus, in order to evaluate the performance of *N*-substituted CHT derivatives for soil release properties, the CHT derivatives pretreated cotton fabrics were subjected to soiling with olive oil, a major component of human sebum, and vacuum cleaner dirt. Evaluations of S.R property performed both gravimetrically by determining percentage soil take up and soil retention; and optically in terms of degree of soiling [56, 57] and yellowness index (Y.I.) presented in Tables 4.38, 4.39 and 4.40 and graphically in Figures 4.40, 4.41 and 4.42.

Of the various analytical techniques employed for the evaluation of soiling tendency, the 'soil retention' characterized the actual amount of impurities (oil +

particulate soil) remained gravimetrically on the fibre. The differences among these values were very less. Hence only an apparent trend in the soiling behaviour was determined. Since small changes in soil retention can greatly alter the optical appearance both gravimetric and optical methods of evaluation were employed for the better understanding of soling behaviour of CHT derivatives treated cotton fabric.




*Conc in pad bath 10 g/L, Mol wt: CHT-D4:20698, CHT: 135,839, CHT-MC: 654,127, DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40*

**Figure 4.40** Effect of different chitosan and *N*- Sub CHT treatment on soiling of cotton fabric

**Table 4.39** Effect of different CHT and *N*- sub CHT treatment on degree of soiling

| Sample | *N*-Alkyl/Aryl CHT treated fabric | | | Sample | *N*-Alkyl/Aryl Q CHT treated fabric | | |
|---|---|---|---|---|---|---|---|
| | $(K/S)_U$ Unsoiled | $(K/S)_S$ Soiled | Degree of Soiling $(K/S)_U$-$(K/S)_S$ | | $(K/S)_U$ Unsoiled | $(K/S)_S$ Soiled | Degree of Soiling $(K/S)_U$-$(K/S)_S$ |
| Control | 0.063 | 0.1852 | 0.122 | Control | 0.063 | 0.1852 | 0.122 |
| CHT-D4 | 0.1464 | 0.4276 | 0.281 | TMCHT 1 | 0.0937 | 0.2742 | 0.181 |
| CHT | 0.1476 | 0.4318 | 0.284 | TMCHT 2 | 0.0846 | 0.2475 | 0.163 |
| CHT-MC | 0.1531 | 0.4478 | 0.295 | TMCHT 3 | 0.0672 | 0.1943 | 0.127 |
| N-Et CHT (1:2) | 0.1479 | 0.4328 | 0.285 | N-EtQ CHT(1:2) | 0.0885 | 0.2589 | 0.170 |
| N-Bu CHT (1:2) | 0.1806 | 0.5184 | 0.348 | N-Bu Q CHT (1:2) | 0.1263 | 0.3696 | 0.243 |
| N-Dod CHT (1:2) | 0.1940 | 0.5676 | 0.374 | N-Dod Q CHT(1:2) | 0.1471 | 0.4303 | 0.283 |
| N-Bz CHT (1:4) | 0.1866 | 0.5459 | 0.354 | N-Bz Q CHT (1:4) | 0.1445 | 0.4228 | 0.278 |
| N-Np CHT (1:4) | 0.1905 | 0.5573 | 0.367 | N-Np Q CHT (1:4) | 0.1398 | 0.4091 | 0.269 |

*Conc in pad bath 10 g/L, Mol wt: CHT-D4:20698, CHT: 135,839, CHT-MC: 654,127, DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40*

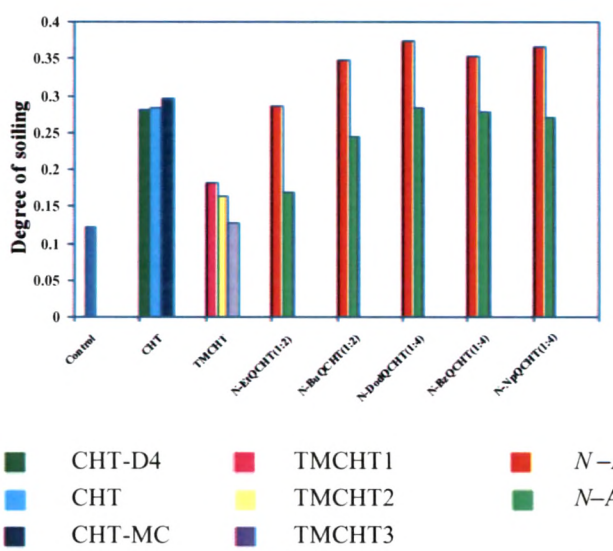



**Figure 4.41** Effect of different CHT and *N*- sub CHT treatment on degree of soiling of cotton

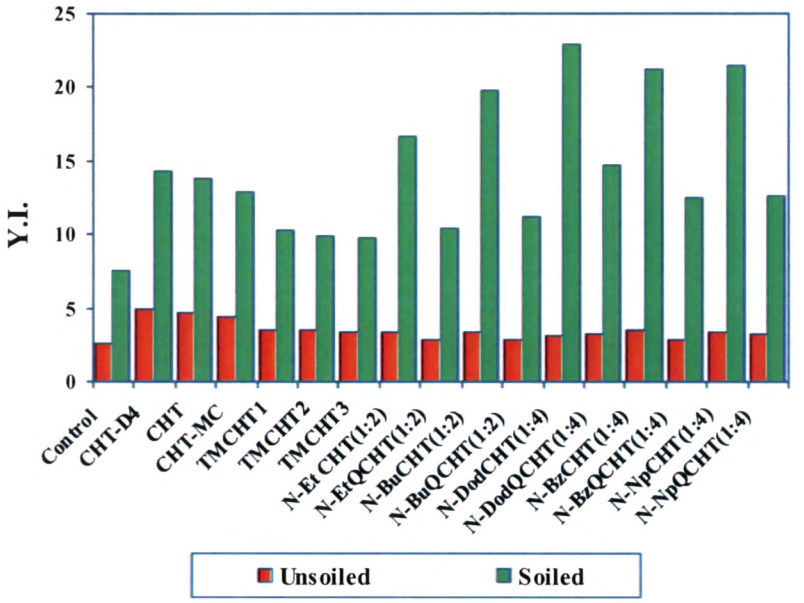
**Table 4.40** Effect of different *N*- sub CHT treatment on yellowness index

| Sample | *N*-Alkyl/Aryl CHT treated fabric | | | Sample | *N*-Alkyl/Aryl Q CHT treated fabric | | |
|---|---|---|---|---|---|---|---|
| | DS, % | $YI_{(U)}$ Unsoiled | $YI_{(S)}$ Soiled | | DS, % | $YI_{(U)}$ Unsoiled | $YI_{(S)}$ Soiled |
| Control | - | 2.63 | 7.61 | Control | - | 2.63 | 7.61 |
| CHT-D4 | - | 4.90 | 14.31 | TMCHT 1 | - | 3.49 | 10.24 |
| CHT | - | 4.69 | 13.75 | TMCHT 2 | - | 3.46 | 9.86 |
| CHT-MC | - | 4.4 | 12.87 | TMCHT 3 | - | 3.35 | 9.83 |
| N-Et CHT (1:2) | 45.5 | 3.34 | 16.72 | N-Et Q CHT(1:2) | 45.5 | 2.85 | 10.48 |
| N-Bu CHT (1:2) | 40.1 | 3.34 | 19.83 | N-Bu Q CHT (1:2) | 40.1 | 2.84 | 11.19 |
| N-Dod CHT (1:2) | 37.6 | 3.07 | 22.91 | N-Dod Q CHT(1:2) | 37.6 | 3.26 | 14.65 |
| N-Bz CHT (1:4) | 44.9 | 3.48 | 21.23 | N-Bz Q CHT (1:4) | 44.9 | 2.88 | 12.49 |
| N-Np CHT (1:4) | 37.6 | 3.37 | 21.52 | N-Np Q CHT (1:4) | 37.6 | 3.28 | 12.66 |

*Conc in pad bath 10 g/L, Mol wt: CHT-D4:20,698; CHT: 135,839; CHT-MC: 654,127; DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40*

It was observed from these results that the chitosan treated samples were soiled greatly than the control one. The molecular weight of chitosan could show little influence of the soil retention, which was increased slightly accordingly. The optical method parameters such as degree of soiling and yellowness index were, however, maximum for low molecular weight chitosan i.e. CHT-D4. This anomaly may be attributed to the comparatively higher yellowness of CHT-D4 acquired during depolymerization of CHT. It was further observed from these results that the soiling tendency of CHT derivative treated samples was increased with increase in chain length or molecular size due to *N*-alkyl or *N*-aryl substituents on chitosan. The quaternization of CHT and these *N*-substituted CHT derivatives was found to improve the soil release properties. The most pronounced effect was noticed with trimethyl chitosan derivative treated cotton fabrics. The soil repellency or release property was progressively improved with increase in its degree of quaternization. Also the soiling effect produced by *N*-alkyl or *N*-aryl groups

was substantially overcome by the quaternization although the effect of molecular size of substituents was sustained.




*Conc in pad bath 10 g/L, Mol wt: CHT-D4:20698; CHT: 135,839; CHT-MC: 654,127; DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40*

**Figure 4.42** Effect of quaternized *N*- sub CHT treatment on yellowness index

The soiling tendency of chitosan may be attributed to its two inherent properties namely the cationic nature and the lipid binding. Soil particulates being negatively charged often get attracted towards positively charged surfaces. It has been well documented that the chitosan macromolecules bind lipids to great extent [80-82]. The interaction between chitosan and oil is not clearly known but it is believed that the nucleophilic amino groups of chitosan can interact with electrophilic carbonyl carbon of ester bridges in oils. The carbonyl carbons being weakly electrophile due to adjacent electron releasing hydrocarbon chains, only weak forces of attraction between oil and amino groups of chitosan is established. Other forces H- bonding between carbonyl oxygen on oils and hydrogen of amino groups on chitosan; and obviously Van der Waal's forces may also contribute to the attachment of lipids onto chitosan.

When the hydrophobicity of chitosan was increased, as observed from Table 4.30, by increasing the hydrocarbon chain length in alkyl group or by increasing the aromatic

rings or hydrocarbon chain in aryl substituents, the possibility of polarization forces are reduced due to these bulkier side groups and the hydrophobic -hydrophobic interaction between *N*-alkyl or *N*-aryl and the hydrocarbon chains of oils is established. These interactions are very much similar to the partial dissolution of hydrocarbon chain of oils into hydrophobic groups of *N*-substituent on chitosan and vise versa due to similar forces of attraction between them quantified by a terminology solubility parameter (δ) [83] and lead to fat binding. Quaternization of chitosan and *N*-substituted chitosan derivatives converts the primary and secondary amines into permanent cations. These ions, due to ion dipole forces, interact with surrounding water molecules in the washing bath and get hydrated. The improved absorbency of cotton fabric treated with quaternized CHT and *N*-substituted CHT derivatives can be seen from the Table 4.30. This improved hydrophilicity facilitates the removal of soil as explained by Erik Kissa's mechanism [84]. According to this, the particulate soil is removed from fibres by a two step process. First, a thin layer of wash liquor penetrates between the particle and the fibre surface, enabling surfactants to adsorb onto particle surface as shown in Figure 4.43. Then, the particle becomes solvated and is transported away from the fibre and is transported away from the fibre and into the bulk of the wash liquid by mechanical action. Thus the modification of chitosan by *N*-alkyl or *N*-aryl substitution for the enhanced/improved handle and antibacterial was needed to be compromised with poor soil release property. The quaternization of these derivatives improved the hydrophilicity of treated fabric and also the soil release properties, yet the discrepancy due to hydrophobic substituents still persist. An extensive research in this domain is in demand.

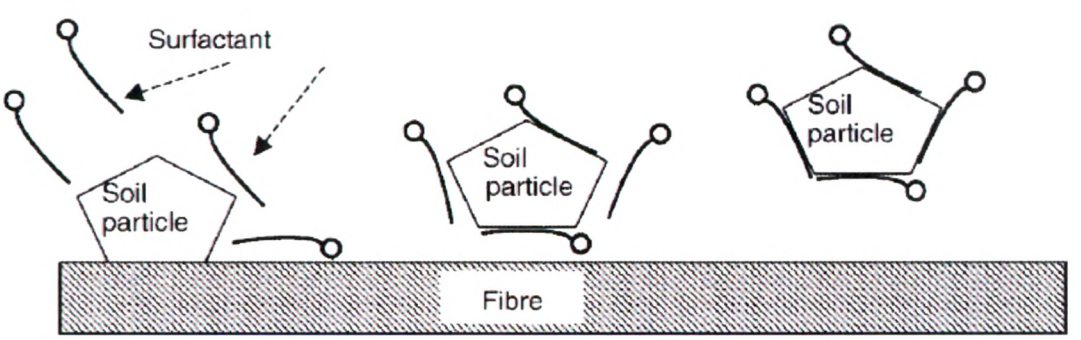



**Figure 4.43** Release of particulate soil from fibre surface

### *4.3.3.10 Effect of N- substituted CHT treatment on resistance against microorganism of cotton fabric*

As discussed in previous chapters, chitosan was found to exhibit antibacterial activity and was improved when scaled down to nano level and in conjunction with nano silver. The CHT, however, has poor solubility at neutral and therefore is almost inactive or weakly active [27]. In fact, the objective of the chitosan derivatives synthesis was to enhance such intrinsic property of chitosan. Thus the effect of quaternization and *N*- alkyl and *N*-aryl substituents of varying molecular size (hydrophobicity) on resistance to microbial attack on cotton fabric substrate was evaluated through soil burial test.

**Table 4.41A** Effect of different *N*- Alkyl/Aryl CHT treatment on resistance against microbial attack of cotton fabric (soil burial test)

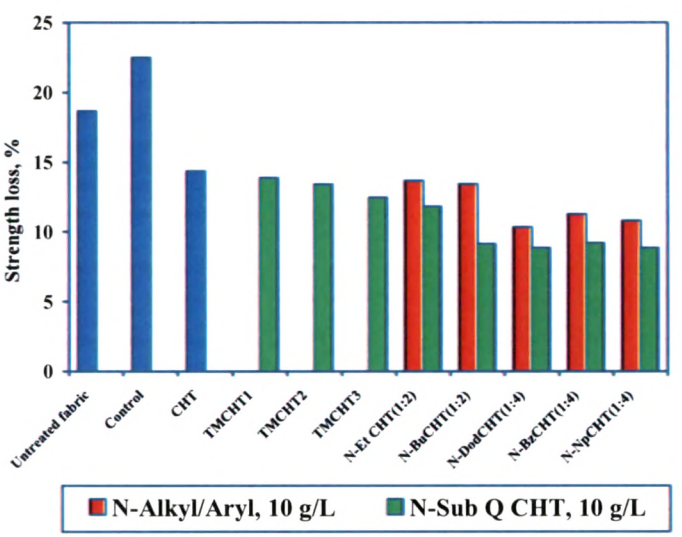
| Sample | DS, % | Tenacity, g/tex | | Strength loss, % | Elongation at break, % | |
|---|---|---|---|---|---|---|
| | | Before soil burial | After soil burial | | Before soil burial | After soil burial |
| Untreated cotton fabric | - | 23.33 | 18.98 | 18.65 | 5.25 | 3.50 |
| Control | - | 20.87 | 18.08 | 22.50 | 5.00 | 3.50 |
| CHT | - | 21.77 | 18.64 | 14.36 | 4.50 | 3.75 |
| N-Et CHT (1:2) | 45.5 | 21.96 | 18.96 | 13.67 | 5.00 | 4.00 |
| N-Bu CHT (1:2) | 40.1 | 21.08 | 18.25 | 13.44 | 4.75 | 4.50 |
| N-Dod CHT(1:4) | 37.6 | 21.88 | 19.61 | 10.36 | 5.25 | 4.50 |
| N-Bz: CHT (1:4) | 44.9 | 22.01 | 19.53 | 11.29 | 5.00 | 5.00 |
| N-Np: CHT (1:4) | 37.6 | 20.53 | 18.31 | 10.83 | 5.00 | 4.75 |

*Conc in pad bath 10 g/L*

**Table 4.41B** Effect of different *N*- Alkyl/Aryl Q CHT treatment on resistance against microbial attack of cotton fabric (soil burial test)

| Sample | DQ, % | Tenacity gm/tex | | Strength loss, % | Elongation, % | |
|---|---|---|---|---|---|---|
| | | Before soil burial | After soil burial | | Before soil burial | Before soil burial |
| Untreated cotton fabric | - | 23.33 | 18.98 | 18.65 | 5.25 | 3.50 |
| Control | - | 20.87 | 18.08 | 22.50 | 5.00 | 3.50 |
| CHT | - | 21.77 | 18.64 | 14.36 | 4.50 | 3.75 |
| TMCHT1 | 13.4 | 21.38 | 18.41 | 13.88 | 4.75 | 4.00 |
| TMCHT2 | 22 | 21.81 | 18.88 | 13.42 | 5.00 | 4.00 |
| TMCHT3 | 50.9 | 21.18 | 18.54 | 12.47 | 4.50 | 4.00 |
| N-Et QCHT (1:2) | 52 | 21.68 | 19.12 | 11.83 | 4.50 | 4.00 |
| N-BuQCHT (1:2) | 47.5 | 20.14 | 18.30 | 9.16 | 5.25 | 4.00 |
| N-DodQCHT(1:4) | 45.1 | 21.36 | 19.47 | 8.87 | 5.00 | 3.75 |
| N-Bz QCHT (1:4) | 41.4 | 21.81 | 19.80 | 9.22 | 4.75 | 4.00 |
| N-NpQCHT (1:4) | 40 | 19.92 | 18.19 | 8.86 | 5.25 | 4.00 |

*Conc in pad bath 10 g/L*




*DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; DS(%)/DQ(%): N-Et QCHT=45.5/52, N- Bu Q CHT (1:2) = 40.1/47.5, N-Dod Q CHT (1:4)= 37.6/45.1, N-Bz Q CHT (1:4)= 44.9/41.4, N-Np Q CHT(1:4)= 37.6/40*

**Figure 4.44** Effect different *N*- sub CHT treatments on resistance against microbial attack of cotton fabric (soil burial test)

It was observed from Tables 4.41 (A &B) and Figure 4.44 that with increase in degree of quaternization the resistance to antimicrobial attack increased. The results revealed that the long chain alkyl group i.e. dodecyl chain and aromatic substituents were more effective than the CHT and quaternary ammonium CHT derivatives for almost same level of DS. When these *N*-substituted CHT derivatives were quaternized, the resistance to microbial attack enhanced. Microbial attack of cellulolytic microflora in a composted soil bed is considered to be the most rigorous and extremely varying depending upon the presence of type of microbes present and the conditions [85]. The action of quaternary ammonium group and the alkyl substituents of CHT on bacteria is associated with the interaction with their cell wall of bacteria [23, 27, 58]. The cell wall is a complex structure and for most of the microbes it is composed of lopopolysaccharide and/or peptidoglycan both having an ionic groups due to phosphates, carboxylates, *N*-acetylmuramic acid etc that can interact with poly cations of CHT derivatives due to quaternary salts. The chelent effect of quaternary salts on divalent cations present on cell wall also contributes to disrupt the integrity of the membrane. In fact, the better antibacterial of quaternary salts cannot rely only on charge density because at acid medium the CHT chain is almost protonated. It is also necessary to consider the degree of ionization and the chain conformation [46]. The chain conformation of quaternized CHT is flexible due to comparatively weaker repulsive forces among quaternary groups than CHT amino groups, which facilitates the interaction with bacteria cell envelope.

The antibacterial property imparted due to the introduction of large hydrophobic moiety on amine group of CHT may be ascribed to the hydrophobic affinity between alkyl chain and phospholipids of bacterial membrane [23, 27, 43, 44, 58]. The phospholipids of bacterial cytoplasmic membrane, besides hydrophilic anionic groups, contain long chain hydrophobic ends of fatty acid tails with carbon number of 12 to 20. Thus, the cationic charge due to quaternized group, hydrophobicity and flexible conformation were found to be important factors in enhancing the antibacterial activity.

The encouraging results of *N*-substitution and quaternization of CHT for antimicrobial activity on undyed cotton fabric inspired to extend the work on dyed fabrics. The performance quaternized and *N*- substituted quaternized CHT derivatives on

dyed cotton fabric for antimicrobial property is presented in Tables 4.42 (A&B) and Figures 4.45 and 4.46.

It was observed from these results that the undyed and dyed blank treated cotton fabrics degraded to maximum extent due to microbial attack. The strength losses were somewhat higher side in dyed fabrics. The influence of post dyeing treatment of *N*- alkyl and *N*-aryl CHT derivatives on microbial attack were found to be nominal where as the post dyeing treatment of CHT and quaternized CHT derivatives showed somewhat deprecation to microbial resistance. The strength losses due to dyeing were more prominent in TMCHT and N-Et Q CHT treated fabric, particularly, on blue dyed fabrics.

**Table 4.42A** Effect of different *N*- Alkyl/Aryl CHT treatment on resistance against microbial attack of dyed cotton fabric (soil burial test)

| Sample | DS, % | C.I. Direct Blue 71 | | | C. I. Direct Red 81 | | |
|---|---|---|---|---|---|---|---|
| | | Tenacity, g/tex | | Strength loss, % | Tenacity, g/tex | | Strength loss, % |
| | | Before soil burial | After soil burial | | Before soil burial | After soil burial | |
| Untreated dyed fabric | - | 22.68 | 18.32 | 19.33 | 22.73 | 18.42 | 18.96 |
| Control (Dyed- blank treated) | - | 20.66 | 15.89 | 23.08 | 20.81 | 16.14 | 22.43 |
| CHT | - | 21.59 | 18.06 | 16.33 | 21.14 | 17.95 | 17.04 |
| N-Et CHT (1:2) | 45.54 | 21.87 | 19.02 | 12.81 | 21.69 | 18.84 | 13.16 |
| N-Bu CHT (1:2) | 40.13 | 22.11 | 19.19 | 13.22 | 21.35 | 18.61 | 13.62 |
| N-Dod CHT(1:4) | 37.63 | 21.64 | 19.33 | 10.88 | 22.23 | 19.27 | 11.29 |
| N-Bz CHT (1:4) | 44.89 | 21.89 | 19.50 | 10.92 | 20.96 | 18.59 | 11.33 |
| N-Np CHT (1:4) | 37.57 | 22.11 | 19.84 | 10.26 | 21.29 | 19.08 | 10.38 |

*Dye 1% o.w.m, Conc of CHT derivatives in pad liquor 10g/L*

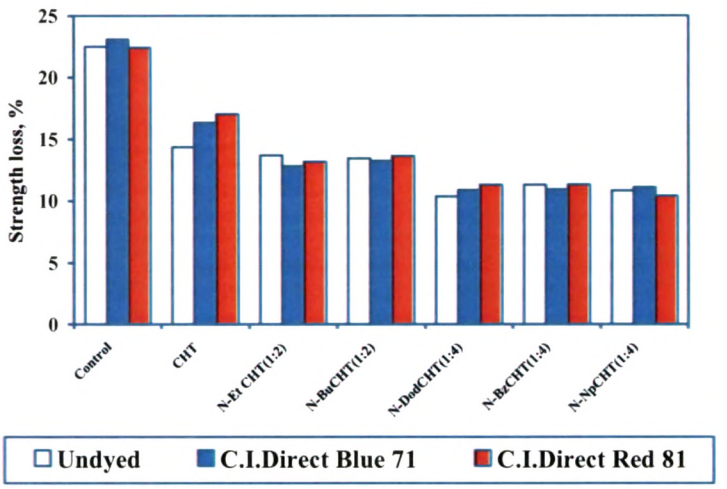
**Table 4.42B** Effect of different *N*- Alkyl/Aryl QCHT treatment on resistance against microbial attack of dyed cotton fabric (soil burial test)

| Sample | DQ, % | C. I. Direct Blue 71 | | | C.I. Direct Red 81 | | |
|---|---|---|---|---|---|---|---|
| | | Tenacity, g/tex | | Strength loss, % | Tenacity, g/tex | | Strength loss, % |
| | | Before soil burial | After soil burial | | Before soil burial | After soil burial | |
| Untreated dyed fabric | - | 22.68 | 18.32 | 19.33 | 22.73 | 18.42 | 18.96 |
| Control (Dyed- blank treated) | - | 20.66 | 15.89 | 23.08 | 20.81 | 16.14 | 22.43 |
| CHT | - | 21.59 | 18.06 | 16.33 | 21.14 | 17.95 | 17.04 |
| TMCHT1 | 13.41 | 21.35 | 18.28 | 14.38 | 21.12 | 18.02 | 14.68 |
| TMCHT2 | 22.43 | 21.66 | 18.60 | 14.12 | 21.33 | 18.38 | 13.85 |
| TMCHT3 | 50.92 | 20.88 | 18.03 | 13.64 | 21.08 | 18.25 | 13.42 |
| N-Et QCHT (1:2) | 51.72 | 22.19 | 19.19 | 12.52 | 21.64 | 18.94 | 12.47 |
| N-Bu QCHT (1:2) | 47.46 | 21.49 | 19.01 | 11.56 | 21.96 | 19.68 | 10.37 |
| N-Dod QCHT(1:4) | 45.00 | 20.93 | 19.14 | 08.56 | 21.48 | 19.41 | 9.63 |
| N-BzQCHT (1:4) | 41.44 | 21.72 | 19.57 | 10.11 | 22.18 | 19.65 | 11.39 |
| N-NpQCHT (1:4) | 39.96 | 22.06 | 19.92 | 9.69 | 21.89 | 19.62 | 10.36 |

*Dye 1% o.w.m, Conc of CHT derivatives in pad liquor 10g/L*

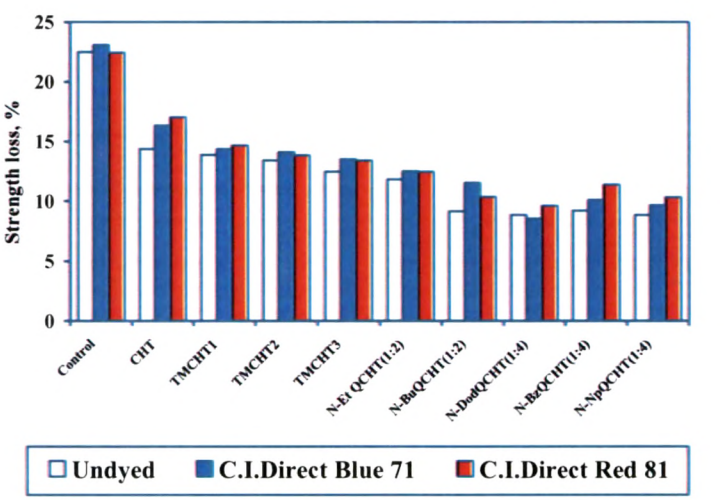
The detrimental effect of dyed fabrics to microbial resistance of quaternized CHT derivatives may be attributed to the neutralization of positive charges with anionic sulphonate groups on direct dyes. Presence of more number of $-SO_3^-$ groups in C. I. Direct Blue 71 than that of red dye, as observed from chemical structures shown in Table 4.1, may be the decline in effectiveness of blue dyed fabric to the microbial resistance. The antibacterial property *N*- sub Q CHT derivatives on dyed fabrics was yet sustained, Figures 4.45 and 4.46, due to *N*- alkyl or *N*-aryl substituents and also to the presence of

excessively large number of cations on Q CHT derivative molecules than the sulphonate anions on dye molecule.




*Dye 1 % o.w.m, Conc in pad bath 10 g/L, DS(%): N-Et CHT=45.5, N- Bu CHT (1:2) = 40.1, N-Dod CHT (1:4)= 37.6, N-Bz CHT (1:4)= 44.9, N-Np CHT(1:4)= 37.6*

**Figure 4.45** Effect different *N*- Alky//Aryl CHT treatments on resistance against microbial attack of dyed cotton fabric (soil burial test)




*Dye 1 % o.w.m, Conc in pad bath 10 g/L, DQ (%): TMCHT1=13.4, TMCHT2=22, TMCHT3= 50.9; N-Et QCHT=52, N- Bu Q CHT (1:2) = 47.5, N-Dod Q CHT (1:4)= 45.1, N-Bz Q CHT (1:4)= 41.4, N-Np Q CHT(1:4)= 40*

**Figure 4.46** Effect different quaternized *N*- sub CHT treatment on resistance against microbial attack of dyed cotton fabric (soil burial test)

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