CHAPTER 2

THEORY

In general, etherification is a preparation process of ethers-organic compounds which contain two groups attached to oxygen. Its general formula is ROR, ArOR or ArOAr

where   R   =   alkyl group

Ar   =   Aryl group

With the presence of alkali reagent, etherification can occur in a system having alcohols, phenols and sugar alcohols (4, 5, 6, 7, 8).

Etherification is frequently and commomly obtained by the reaction between alkyl halide (or substituted alkyl halide) with sodium alkoxide or sodium phenoxide as shown in the following equation (5).

$$RONa + RX \longrightarrow ROR + NaX$$

With the presence of alkali, etherification of cellulose can evidently occur by the reaction of cellulose with etherifying agents such as organic halides, alkene oxides, or olefin activated by polar substituent groups (1, 7).

As previously mentioned, cellulose alone does not react with etherifying agent. Since there are 3 hydroxyl groups in each glucose unit within cellulose chain, such hydroxyl groups must be activated by alkali treatment to form alkali cellulose which is able to undergo further etherification (1, 7).

Theoretically, the action of alkali on cellulose or alkali cellulose formation may proceed in accordance with 2 different schemes (4):

(a) Cellulose forms true alcoholates with alkali metal which replaces the hydrogen ion as in other monohydric and polyhydric alcohols:

$$RCell(OH)_3 + NaOH \longrightarrow RCell(OH)_2 \cdot ONa + H_2O$$

(b) A molecular or addition compound is formed in such a way that molecules of alkali are added to the hydroxyl groups of cellulose:

$$RCell(OH)_3 + NaOH \longrightarrow RCell(OH)_2 \cdot OH \cdot NaOH$$

However, there is, at present, no direct proof that either of these compounds is in fact formed but the composition of alkali cellulose depends on several factors listed below as mentioned by N.I. Nikitin (4):

- concentration of alkali

- temperature of the alkali treatment

- nature of the hydroxide employed

- individual properties of the starting cellulose

and

- identity of the medium in which the alkali has been dissolved

According to scheme (a), alcoholates are hydrolysed even in the presence of small amounts of water as pointed out by Rogovin (4, 9). In a separate work, J. Chedin and A. Tribot reported that there is almost no etherification in the absence of water (10). This contradiction was clarified by the latter group that water was a solvating agent acting as a solvent and carrier for the sodium hydroxide, as an agent to swell and solvate the cellulose so that the etherifying agent penetrates readily, and as a diluent for the etherifying agent (1, 10). N.I. Nikitin also cited out that alkali cellulose may be practically made in various reaction media such as aqueous solution, alcoholic solution and other nonaqueous solution (4). However, the rate of

hydrolysis of alkali compound considerably decreases if alcoholic solution is used rather than an aqueous solution (4, 6, 9, 11).

As regard to scheme (2), Webber, Ashar and Champetier found that the amount of bound alkali is much larger in nonaqueous solutions than in aqueous solution (4). They also found that the small amounts of water which are added to certain higher alcohol produce the increasing in the sorption of NaOH and that the rate of establishment of equilibrium in nonaqueous solution is exceeding slow. According to the results obtained from their work, they may indicate that the composition of alkali cellulose is also affected by factors other than the relative rate of formation and hydrolysis of alkali compounds (4, 12).

Under separate work, G.A. Petropavlovskii and N.I. Nikitin found that the increasing of temperature increased the reaction rate (13). They also suggested that the heat involved during mixing must be controlled to prevent the loss of degree of polymerization since cellulose is a high polymer consisting of glucose units linked in long chain by polymerization.

The extent of etherification is commomly considered by determining the degree of substitution (D.S.) of the product obtained. In a cellulose derivative, D.S. is defined as the average number of hydroxyl groups substituted per anhydroglucose unit. Theoretically, the maximum D.S. is 3 as regard to the total number of hydroxyl groups containing in each glucose unit in the cellulose chain (14).

Most of the works reported were conducted by simply using single reaction medium. The addition of organic solvents such as alcohol to the reaction mixture was recently proposed in order to eliminate dough (15).

Eiji Hayakawa and Yazaemon Marita used water miscible or water immiscible organic solvents to increase the D.S. (16).

A certain etherification of alkali cellulose in which either chloroacetic acid or sodium chloroacetate is used as etherifying agent is known as carboxymethylation (1). Timell and Rydholm showed that the substitution can be first taken place at the 6th position for its D.S. approximately up to 0.15 and then the secondary hydroxyls at 2nd and 3rd positions begin to participate in reaction (4, 17, 18).

The carboxymethylation equation is generally expressed as :

$$RCell(OH)_3 + ClCH_2COONa + NaOH \rightleftharpoons RCell(OH)_2OCH_2COONa$$
$$+ NaCl + H_2O \qquad (1)$$
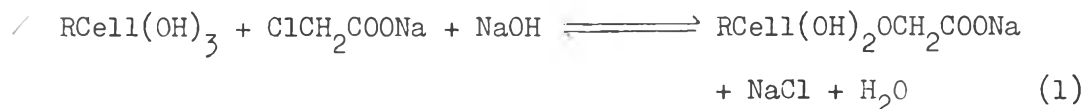
The D.S. of the product and also its solubility depends upon the reaction conditions used. Yehia Fahmy and Olfat Mansour pointed out that the products with minimum D.S. of about 0.4 are water soluble and ones with D.S. lower than 0.4 are almost dilute - alkali soluble(19). They also suggested that apart from the main reaction of carboxymethylation (see equation 1), the sodium chloroacetate is hydrolysed to sodium glycolate as followed :

$$ClCH_2COONa + NaOH \rightleftharpoons HOCH_2COONa + NaCl \qquad (2)$$

This side reaction is induced by enhancing reaction-variables which hence adversely influence the rate of the main reaction of etherification of cellulose.

The influence of reaction variables on the D.S. and the alkali solubility and on the reactivity was studied by R.R. McLauglin and J.H.E. Herbst in 1950 (20). They found that the efficiency of carboxy-

methylation could be improved by lower reaction temperature, decreasing excess sodium hydroxide and by increasing time.

Considering equation (1), Matao Nakamura and Koichiro Watanabe suggested that the expression is also true for the following form (21) :

$$RCell(OH)_3 + xClCH_2COONa + xNaOH \rightleftharpoons RCell(OH)_{3-x}(OCH_2COONa)_x$$
$$+ xNaCl + xH_2O \qquad (3)$$
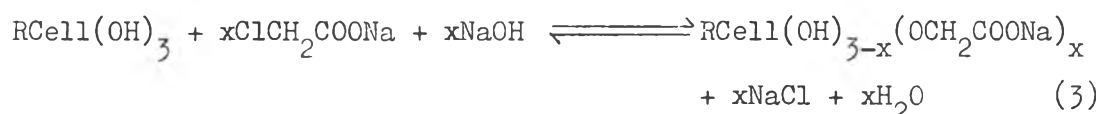
where x = degree of substitution

As we know, the extent of etherification is commomly considered by determining the D.S. of the product obtained. It is worthwhile to present here with such detail.

Determination of degree of substitution

a) Determination of moisture content.

In order to obtain the exact weight of the product used for calculating the D.S., the moisture content must be first determined.

The moisture content can be calculated by using the following equation (14):

percentage of moisture = (A/B) (100)

where A   = mass loss on drying

B   =grams of sample used

In practice, dry m grams of product for about 5 hours in vacuum dryer. After cooling, find the weights of sample before and after drying.
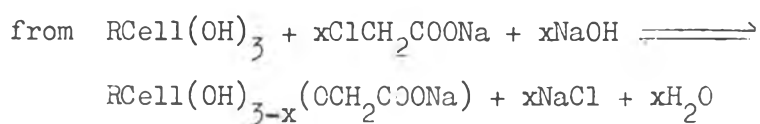
Let m   = weight of sample

a   = weight of nickel crucible and its cover

b   = weight of nickel crucible, cover and sample after drying

Therefore, percentage of moisture = $\left\{ \dfrac{(m + a) - b}{m} \right\}(100)$ $\qquad (4)$

b) Determination of D.S.

The quantity of sodium in the etherification product can be calculated as followed :

from $RCell(OH)_3 + xClCH_2COONa + xNaOH \rightleftharpoons$

$RCell(OH)_{3-x}(OCH_2COONa) + xNaCl + xH_2O$

The percentage of sodium is given by the equation

$$\% \ Na = \frac{(23x)(100)}{162 + 80x} \qquad (5)$$

where

$RCell(OH)_3$ is taken as the formula of the anhydroglucose unit $(C_6H_7O_2(OH)_3)$. Its molecular weight is 162.

x is degree of substitution (D.S.) which is the average number of hydroxyl groups substituted per anhydroglucose unit.

$RCell(OH)_{3-x}(OCH_2COONa)_x$ is the etherification product having molecular weight $162 + 80x$.

$$\text{Therefore,} \quad x = \frac{(162)(\%Na)}{2300 - (80)(\%Na)} \qquad (6)$$