

CHAPTER 3

Theoretical Analysis



3.1 Introduction

Cotton yarn mercerization is a process which is used for improving the strength of the cotton yarn and also improving the lustre of the cotton yarn. The process was studied many years ago but scientist cannot describe clearly the mechanism of diffusion of sodium ions in the cotton fibres. The research was performed in holland (1, 2) to study the effect the sodium hydroxide on the cotton fibres at various concentrations, it was concluded that the amount of sodium ions that diffuses through the cotton fibres depend on the viscosity of the sodium hydroxide solution, the degree of swelling of the fibres, the time and the tension. The result was shown in Eq (2.2).

3.2 Chemical Reaction

Mercerization is a chemical reaction between sodium ions and cellulose (Polyanhydroglucose) of the cotton fibres. Neale made a valuable contribution to understand the swelling of the cotton by alkalis (4), by the mathematical formulation of a theory based on the Donnan Membrane Equilibrium. In this theory, cellulose is assumed to behave as a weak monobasic acid with a molecular weight equal to that of the single chain unit. The reaction can be

written as shown below.



Eq. (3.1) shows that under alkali condition, cotton is in alkali-cellulose form and under acidic condition, cotton is in cellulose form.

3.3 Expanding Product and Shrinking Core Model

To determine the rate of mercerization, the mathematical model was developed in accordance with expanding product and shrinking core model(3). In this model, cotton fibre is assumed to be a cylinder of radius r_s , it is in contact with sodium hydroxide solution whose bulk concentration is C_b . Consider the case where the temperature is uniform throughout the heterogeneous region. As reaction occurs a layer of product alkali-cellulose, GluONa, forms around the unreacted core of cellulose. It is supposed that this layer is porous because it is expanded inwards to the center of the fibre, so that reaction occurs by diffusion of sodium ions through the layer of alkali cellulose to react at the interface between alkali cellulose and unreacted core. This situation is shown in Fig. 3.1 where the concentration of sodium ions are labeled at various location. The shape of the concentration profile from bulk liquid to reacting surface is also indicated.

One more restriction must be placed on the system before a simple mathematical analysis is feasible, the rate of movement

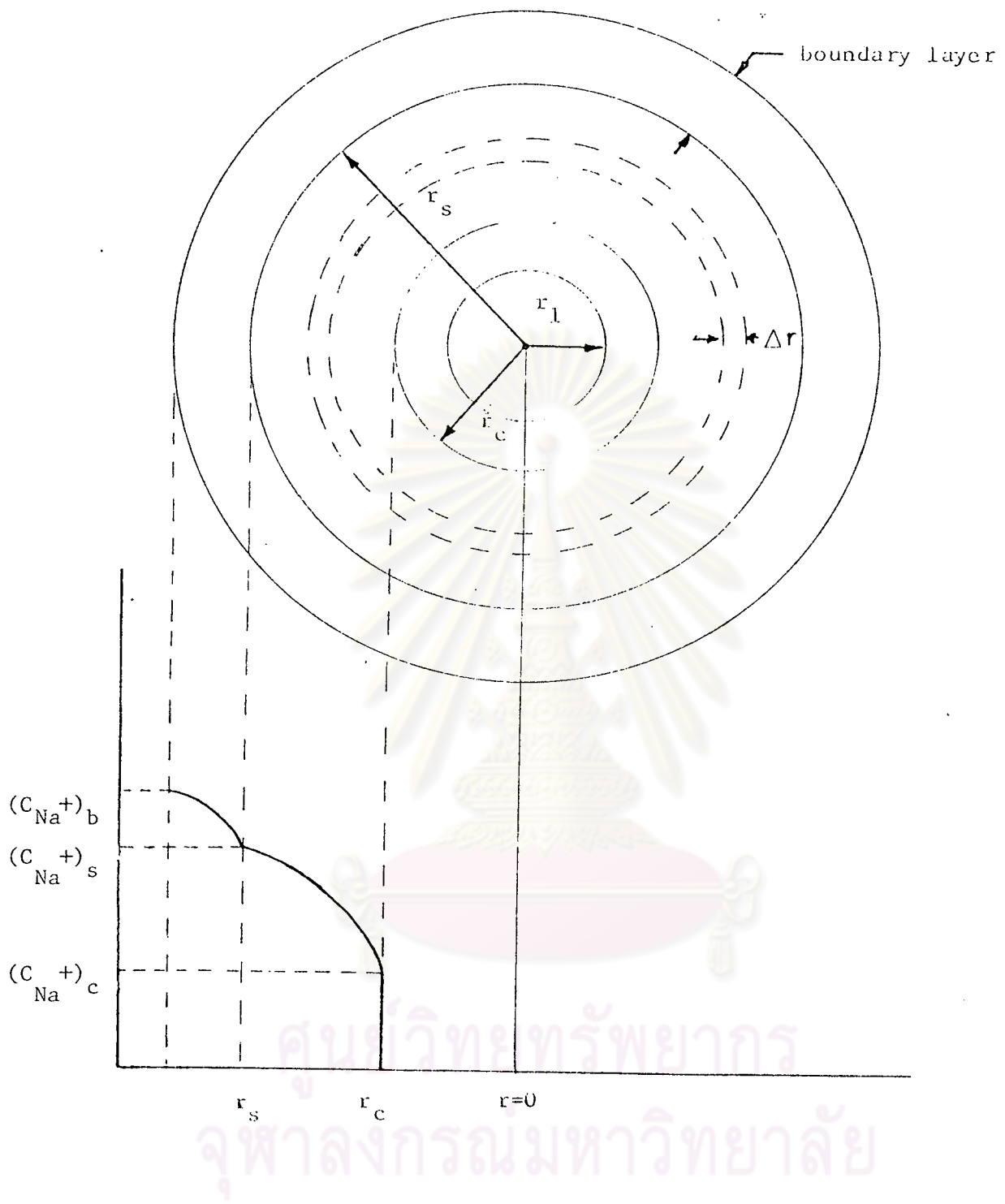


Fig 3.1 Concentration profile in a cylindrical fibre

of the reaction interface at r_c that is dr_c/dt is small with respect to the velocity of the diffusion of sodium ions through the product layer.

Granting pseudo-steady-state conditions, the three rates, diffusion of Na^+ through boundary layer, diffusion through the layer of product, and reaction at the interface are identical. By equating the expression for each of these processes, the concentration $(C_{\text{Na}^+})_c$ can be expressed in terms of the known $(C_{\text{Na}^+})_b$ and the radius of the unreacted core r_c . The three rate equations expressed as moles of Na^+ disappearing per unit time per unit length of cotton fibre, are

$$-\frac{dN_{\text{Na}^+}}{dt} = 2\pi r_s k_m \left\{ (C_{\text{Na}^+})_b - (C_{\text{Na}^+})_s \right\} \quad (3.2)$$

for external diffusion,

$$-\frac{dN_{\text{Na}^+}}{dt} = 2\pi r_c D_e \left(\frac{dC_{\text{Na}^+}}{dr} \right)_{r=r_c} \quad (3.3)$$

for diffusion through product, and

$$-\frac{dN_{\text{Na}^+}}{dt} = 2\pi r_c k (C_{\text{Na}^+})_c \quad (3.4)$$

for reaction at r_c .

In Eq. (3.2), k_m is the external mass transfer coefficient. The rate through the product layer, Eq (3.3), is evaluated at $r = r_c$; D_e is the effective diffusivity of Na^+ through this porous layer. In writing Eq (3.4), the chemical reaction at r_c is assumed to be first order in Na^+ and irreversible. It is also taken as directly proportional to the outer surface area of unreacted core cellulose.

To evaluate the gradient in Eq (3.3) consider the diffusion of Na^+ through the layer of alkali-cellulose. With the pseudo-steady-state assumption, this process can be evaluated independently of the change in r_c . Consider a small element thickness Δr at location r in the product layer (Fig. 3.1), the steady state mass balance of Na^+ around this layer is

$$-\left(2\pi r D_e \frac{dC_{\text{Na}^+}}{dr}\right)_r + \left(2\pi r D_e \frac{dC_{\text{Na}^+}}{dr}\right)_{r+\Delta r} = 0 \quad (3.5)$$

Taking the limit as $\Delta r \rightarrow 0$ gives

$$\frac{d}{dr} \left(r D_e \frac{dC_{\text{Na}^+}}{dr} \right) = 0 \quad (3.6)$$

Eq (3.6) is integrated twice, with the boundary conditions

$$C_{\text{Na}^+} = (C_{\text{Na}^+})_s \quad \text{at} \quad r = r_s$$

$$C_{\text{Na}^+} = (C_{\text{Na}^+})_c \quad \text{at} \quad r = r_c$$



used to evaluate the integrating constant, the result is

$$C_{Na^+} - (C_{Na^+})_s = \left\{ (C_{Na^+})_s - (C_{Na^+})_c \right\} \frac{\ln\left(\frac{r}{r_s}\right)}{\ln\left(\frac{r_s}{r_c}\right)} \quad (3.7)$$

The concentration profile through the product layer may be calculated by differentiating Eq. (3.7) with respect to r and then set the boundary at $r = r_c$ to give

$$\left(\frac{dC_{Na^+}}{dr} \right)_{r=r_c} = \left\{ (C_{Na^+})_s - (C_{Na^+})_c \right\} \frac{1}{r_c \ln\left(\frac{r_s}{r_c}\right)} \quad (3.8)$$

Substituting Eq (3.8) in Eq (3.3) gives

$$-\frac{dN_{Na^+}}{dt} = \frac{2\pi D_e}{\ln\left(\frac{r_s}{r_c}\right)} \left\{ (C_{Na^+})_s - (C_{Na^+})_c \right\} \quad (3.9)$$

Now $(C_{Na^+})_s$ and dN_{Na^+}/dt can be eliminated from Eqs. (3.2), (3.4) and (3.9) to give $(C_{Na^+})_c$ in terms of $(C_{Na^+})_b$ and r_c . The result is

$$(C_{Na^+})_c = \frac{(C_{Na^+})_b}{\left\{ 1 + \frac{k}{D_e} r_c \ln\left(\frac{r_s}{r_c}\right) + \frac{k}{k_m} \cdot \frac{r_c}{r_s} \right\}} \quad (3.10)$$

Substituting $(C_{Na^+})_c$ in Eq. (3.4) gives the global rate in term of $(C_{Na^+})_b$ and r_c

$$\left. \begin{array}{l} \text{Rate per unit length} \\ \text{of cotton fibre} \end{array} \right\} = - \frac{dN_{Na^+}}{dt} = \frac{2r_c k (C_{Na^+})_b}{\left\{ 1 + \frac{k}{D_e} r_c \ln \frac{r_s}{r_c} + \frac{k}{k_m} \cdot \frac{r_c}{r_s} \right\}} \quad (3.11)$$

Since r_c is a variable, Eq. (3.11) is not useful until we express r_c as a function of time.

According to the cylindrical geometry of cotton fibre, the rate of reaction of cotton fibre (mole per unit time per unit length of cotton fibre) may be written as the following.

$$\begin{aligned} - \frac{dN_{Na^+}}{dt} &= - \frac{dN_{GLuOH}}{dt} = \frac{dN_{GLuONa}}{dt} \\ &= \frac{d}{dt} \left\{ \left(\frac{\rho}{M} \right)_{GLuONa} \left(r_s^2 - r_c^2 \right) \right\} \\ &= - \left(\frac{\rho}{M} \right)_{GLuONa} \left(2r_c \frac{dr_c}{dt} \right) \end{aligned} \quad (3.12)$$

$$= - 2r_c \left(\frac{\rho}{M} \right)_{GLuONa} \cdot \frac{dr_c}{dt} \quad (3.13)$$

Eq. (3.4) = Eq. (3.13) gives

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$$-\frac{dr_c}{dt} = k \left(\frac{M}{\rho} \right)_{\text{GLuONa}} \cdot (C_{\text{Na}^+})_c \quad (3.14)$$

Substituting Eq (3.10) in Eq. (3.14) provides a differential equation whose solution gives $r_c = f(t)$

$$-\frac{dr_c}{dt} = \frac{k(M/\rho)_{\text{GLuONa}} (C_{\text{Na}^+})_b}{\left\{ 1 + \frac{k r_c}{De} \ln \frac{r_s}{r_c} + \frac{k}{k_m} \cdot \frac{r_c}{r_s} \right\}} \quad (3.15)$$

Combining Eq. (3.11) and Eq. (3.15) together provides the global rate in term of $(C_{\text{Na}^+})_b$ and time. If Eq. (3.15) is integrated the result will depend on $(C_{\text{Na}^+})_b$ which varies with time as in some types of reactor. In this experiment, $(C_{\text{Na}^+})_b$ will be kept constant by using both high velocity stirring and excess sodium hydroxide.

If $(C_{\text{Na}^+})_b$ is constant, Eq. (3.15) is easily integrated, starting with $r = r_s$ at $t = 0$

$$-k(C_{\text{Na}^+})_b \left(\frac{M}{\rho} \right)_{\text{GLuONa}} \int_0^t dt = \int_{r_s}^{r_c} \left\{ 1 + \frac{kr_c}{De} \ln \frac{r_s}{r_c} + \frac{k}{k_m} \cdot \frac{r_c}{r_s} \right\} dr_c \quad (3.16)$$

It is convenient to express the result in terms of a dimensionless time

$$t^* = \left(\frac{M}{\rho} \right)_{\text{GLuONa}} \cdot \frac{k(C_{\text{Na}^+})_b}{r_s} \cdot t \quad (3.17)$$

and two groups relating the diffusion and reaction resistances

$$Y_1 = \frac{D_e}{k_m r_s} = \frac{\text{external diffusion resistance}}{\text{diffusion resistance in product layer}} \quad (3.18)$$

$$Y_2 = \frac{k r_s}{D_e} = \frac{\text{diffusion resistance in product layer}}{\text{reaction resistance at } r_c} \quad (3.19)$$

Integrating Eq. (3.16) gives

$$t^* = \left(1 - \frac{r_c}{r_s}\right) \left\{ 1 + \frac{1}{2} \left(1 + \frac{r_c}{r_s}\right) \left(\frac{y_2}{2} + y_1 y_2\right) \right\} + \frac{y_2}{2} \left(\frac{r_c}{r_s}\right)^2 \ln \frac{r_c}{r_s} \quad (3.20)$$

Eq. (3.20) is in term of $\frac{r_c}{r_s}$ which is difficult to be detected, the ratio $\frac{r_c}{r_s}$ can be converted into $\frac{r_1}{r_{1,i}}$ by taking material balance. Fig (3.2) shows the cross section of cotton fibre at various stages of mercerization. Before mercerization ($t = 0$), external radius of cotton fibre is r_s , internal radius is $r_{1,i}$ and initial density is ρ_i . When it is mercerized to a certain level ($t=t$), its external radius is still r_s but its internal radius decreases to r_1 and density divided into two zones, outer zone is ρ_f and inner zone is ρ_i , when the mercerization time approaches infinite, full mercerization, external radius also doesnot change while internal radius $r_{1,f}$ approaches zero and final density is ρ_f .

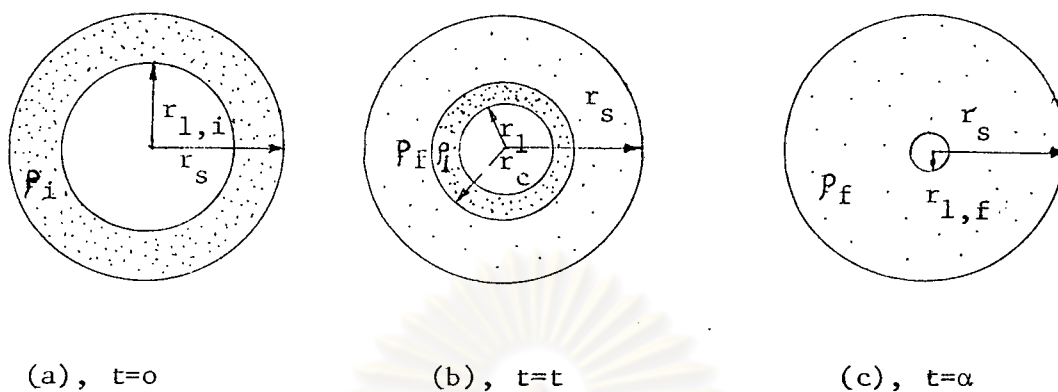


Fig. (3.2) Cross section of cotton fibre (a) before mercerized
(b) partial mercerized (c) full mercerized.

Mass of cotton fibre at any step of mercerization has the same amount and can be calculated as the following.

$$\text{when } t = 0 \quad M = \rho_i V_i = \rho_i \pi (r_s^2 - r_{l,i}^2) \quad (3.21)$$

$$t = t \quad M = \rho_f \pi (r_s^2 - r_c^2) + \rho_i \pi (r_c^2 - r_l^2) \quad (3.22)$$

$$= \pi \rho_i \left\{ \frac{\rho_f}{\rho_i} (r_s^2 - r_c^2) + (r_c^2 - r_l^2) \right\} \quad (3.23)$$

$$t = \alpha \quad M = \rho_f V_f = \rho_f \pi (r_s^2 - r_{l,f}^2) \quad (3.24)$$

Eq. (3.21) = Eq. (3.23) = Eq. (3.24), by solving these equations gives.

$$\frac{r_c}{r_s} = \sqrt{\frac{r_1^2 - r_{1,f}^2 + \left(\frac{r_{1,f}}{r_s}\right)^2 (r_{1,i}^2 - r_1^2)}{r_{1,i}^2 - r_{1,f}^2}} \quad (3.25)$$

If $r_{1,f} \rightarrow 0$, Eq (3.25) becomes

$$\frac{r_c}{r_s} = \frac{r_1}{r_{1,i}} \quad (3.26)$$

Substituting Eq. (3.26) in Eq. (3.20) gives

$$t^* = \left(1 - \frac{r_1}{r_{1,i}}\right) \left\{ 1 + \frac{1}{2} \left(1 + \frac{r_1}{r_{1,i}}\right) \left(\frac{y_2}{2} + y_1 y_2\right) \right\} + \frac{y_2}{2} \left(\frac{r_1}{r_{1,i}}\right)^2 \ln \frac{r_1}{r_{1,i}} \quad (3.27)$$

For the liquid-phase velocity relative to that of the solid particle is high, as in a stirred-reactor, external-diffusion resistance may be negligible. Also, for a highly porous product layer, diffusion resistance through the product may be small. Under such conditions, the rate is chemical reaction control and $y_2 \rightarrow 0$ the Eq. (3.27) reduced to

$$t^* = 1 - \frac{r_1}{r_{1,i}} \quad (3.28)$$



Converting t^* into t gives

$$t = \left(\frac{\rho}{M} \right)_{\text{GLuONa}} \frac{r_s}{k (C_{\text{Na}^+})_b} \left(1 - \frac{r_1}{r_{1,i}} \right) \quad (3.29)$$

For rapid chemical reactions at the interface and a low D_e , the rate is diffusion control. If this is the case, $y_1 \rightarrow 0$, y_2 is large, and Eq. (3.27) becomes

$$\begin{aligned} t^* &= \left(1 - \frac{r_1}{r_{1,i}} \right) \left\{ 1 + \frac{1}{2} \left(1 + \frac{r_1}{r_{1,i}} \right) \left(\frac{y_2}{2} \right) \right\} + \frac{y_2}{2} \left(\frac{r_1}{r_{1,i}} \right)^2 \ln \frac{r_1}{r_{1,i}} \\ &= \left(1 - \frac{r_1}{r_{1,i}} \right) + \frac{y_2}{4} \left\{ 1 - \left(\frac{r_1}{r_{1,i}} \right)^2 \left[1 - \ln \left(\frac{r_1}{r_{1,i}} \right)^2 \right] \right\} \end{aligned} \quad (3.30)$$

converting t^* into t gives

$$t = \left(\frac{\rho}{M} \right)_{\text{GLuONa}} \frac{r_s}{(C_{\text{Na}^+})_b} \left[\frac{1}{k} \left(1 - \frac{r_1}{r_{1,i}} \right) + \frac{r_s}{4D_e} \left\{ 1 - \left(\frac{r_1}{r_{1,i}} \right)^2 \left(1 - \ln \left(\frac{r_1}{r_{1,i}} \right)^2 \right) \right\} \right] \quad (3.31)$$

If it is diffusion control, D_e is much smaller than k . Eq (3.31) can be reduced to

$$t = \left(\frac{\rho}{M} \right)_{\text{GLuONa}} \frac{r_s^2}{4D_e (C_{\text{Na}^+})_b} \left[1 - \left(\frac{r_1}{r_{1,i}} \right)^2 \left\{ 1 - \ln \left(\frac{r_1}{r_{1,i}} \right)^2 \right\} \right] \quad (3.32)$$

3.4 Determination of Rate Constant and/or Effective Diffusivity

If the rate is controlled by chemical reaction at the interface, rate constant can be determined from Eq. (3.29) which the relationship between t and $(1 - \frac{r_1}{r_{1,i}})$ will be linear. From this slope, k can be calculated as the following.

$$\text{slope} = \left(\frac{\rho}{M} \right)_{\text{GLuONa}} \frac{r_s}{k (C_{\text{Na}^+})_b} \quad (3.33)$$

$$\text{or } k = \left(\frac{\rho}{M} \right)_{\text{GLuONa}} \frac{r_s}{(\text{slope}) (C_{\text{Na}^+})_b} \quad (3.34)$$

If the rate is controlled by diffusion of sodium ion through the product layer. The effective diffusivity can be determined from Eq. (3.32) which the relationship between t and $1 - \left(\frac{r_1}{r_{1,i}} \right)^2$ will be linear. From this slope, D_e can be calculated as the following.

$$\text{slope} = \left(\frac{\rho}{M} \right)_{\text{GLuONa}} \frac{r_s^2}{4D_e (C_{\text{Na}^+})_b} \quad (3.35)$$

$$\text{or } D_e = \left(\frac{\rho}{M} \right)_{\text{GLuONa}} \frac{r_s^2}{4 (\text{slope}) (C_{\text{Na}^+})_b} \quad (3.36)$$

3.5 Determination of Conversion

Eq. (3.29) and Eq. (3.32) can be converted into term of conversion (x) by relating $\left(\frac{r_1}{r_{1,i}}\right)^2$ with x and then substituting $\left(\frac{r_1}{r_{1,i}}\right)^2$ with x in Eqs. (3.29) and (3.32) as the following.

$$\begin{aligned}
 \text{Defining conversion } = x &= \frac{M_o - M}{M_o} \\
 &= \frac{\eta(r_s^2 - r_{1,i}^2)\rho_i - \eta(r_c^2 - r_{1,i}^2)\rho_i}{\eta(r_s^2 - r_{1,i}^2)\rho_i} \\
 &= 1 - \left(\frac{r_c^2 - r_{1,i}^2}{r_s^2 - r_{1,i}^2}\right)
 \end{aligned} \tag{3.37}$$

and

$$\frac{r_c}{r_s} = \frac{r_1}{r_{1,i}}$$

then

$$x = 1 - \left(\frac{r_1}{r_{1,i}}\right)^2$$

or

$$\left(\frac{r_1}{r_{1,i}}\right)^2 = 1 - x \tag{3.38}$$

If the rate of reaction is controlled by chemical reaction, when we substitute Eq (3.38) in Eq. (3.29), it gives

$$t = \left(\frac{\rho}{M}\right)_{\text{GLuONa}} \frac{r_s}{k (C_{\text{Na}^+})_b} (1 - \sqrt{1-x}) \tag{3.39}$$

If the rate of reaction is controlled by diffusion of sodium ions through the product layer, when we substitute Eq. (3.38) in Eq. (3.32), it gives

$$t = \left(\frac{\rho}{M}\right)_{\text{GLuONa}} \frac{r_s^2}{4D_e (C_{\text{Na}^+})_b} \left\{ x + (1-x) \ln(1-x) \right\} \quad (3.40)$$

3.6 Determination of Rate of Mercerization

In case of the rate is controlled by chemical reaction, Eq. (3.29) is converted into term of r_c/r_s and it is differentiated with respect to t to find dr_c/dt , this result is substituted in Eq. (3.13) to obtain the rate in terms of k and $(C_{\text{Na}^+})_b$ as the following.

Eq. (3.29) is converted into term of r_c/r_s , it gives

$$t = \left(\frac{\rho}{M}\right)_{\text{GLuONa}} \frac{r_s}{k (C_{\text{Na}^+})_b} \left(1 - \frac{r_c}{r_s}\right) \quad (3.41)$$

Eq. (3.41) is differentiated with respect to t , the result is

$$\frac{dt}{dt} = \left(\frac{\rho}{M}\right)_{\text{GLuONa}} \frac{1}{k (C_{\text{Na}^+})_b} \left(-\frac{dr_c}{dt}\right)$$

Rearrangement.

$$\frac{dr_c}{dt} = -\left(\frac{M}{\rho}\right)_{\text{GLuONa}} k (C_{\text{Na}^+})_b \quad (3.42)$$

Substituting Eq. (3.42) in Eq. (3.13) gives

$$\begin{aligned} -\frac{dN_{\text{Na}^+}}{dt} &= 2r_c k (C_{\text{Na}^+})_b & (3.43) \\ &= \text{Rate per unit length of cotton fibre} \end{aligned}$$

In case of the rate is controlled by diffusion of sodium ion through the product layer, Eq. (3.32) is converted into term of r_c/r_s and it is differentiated with respect to t to find dr_c/dt , this result is substituted in Eq. (3.13) to obtain the rate in terms of D_e , $(C_{\text{Na}^+})_b$ and $r_1/r_{1,i}$ as the following.

Eq. (3.32) is converted into term of r_c/r_s , gives

$$t = \left(\frac{\rho}{M}\right)_{\text{GLuONa}} \frac{r_s^2}{4D_e (C_{\text{Na}^+})_b} \left[1 - \left(\frac{r_c}{r_s}\right)^2 \left\{ 1 - \ln \left(\frac{r_c}{r_s}\right)^2 \right\} \right] \quad (3.44)$$

Eq. (3.44) is differentiated with respect to t , the result is

$$\frac{dt}{dt} = -\left(\frac{\rho}{M}\right)_{\text{GLuONa}} \frac{r_s^2}{4D_e (C_{\text{Na}^+})_b} \left[-2 \frac{r_c}{r_s} \left\{ 1 - \ln \left(\frac{r_c}{r_s}\right)^2 \right\} \right] \frac{dr_c}{dt}$$

Rearrangement

$$\frac{dr_c}{dt} = \left(\frac{M}{\rho}\right)_{\text{GLuONa}} \frac{D_e (C_{\text{Na}^+})_b}{r_c \ln \frac{r_c}{r_s}} \quad (3.45)$$

Substituting Eq. (3.45) in Eq. (3.13) gives

$$-\frac{dN_{\text{Na}^+}}{dt} = \frac{-2D_e (C_{\text{Na}^+})_b}{\ln \frac{r_c}{r_s}} \quad (3.46)$$

Converting Eq. (3.46) into term of $r_1/r_{1,i}$ gives

$$-\frac{dN_{\text{Na}^+}}{dt} = \frac{-2D_e (C_{\text{Na}^+})_b}{\ln \frac{r_1}{r_{1,i}}} \quad (3.47)$$

= Rate per unit length of cotton fibre

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