

Sulfation Kinetics in the Preparation of Cellulose Sulfate*

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Abstract In the established apparatus, the conversion ratios of cellulose sulfation (X) under different sulfation conditions were measured. The range of temperature was from $-5\text{ }^{\circ}\text{C}$ to $+5\text{ }^{\circ}\text{C}$, and the H_2SO_4 concentration was from $3.1\text{ mol}\cdot\text{L}^{-1}$ to $4.5\text{ mol}\cdot\text{L}^{-1}$. The experimental results were used for the establishment of the kinetic model for cellulose sulfation. With the model, X values and the yield of NaCS (Y) can be calculated, thus the reaction with respect to H_2SO_4 concentration is determined to be third order.

Keywords kinetic model, cellulose sulfate, microcapsule

1 INTRODUCTION

A new developed microcapsule system^[1–7] is composed of sodium cellulose sulfate (NaCS) and poly-diallyl-dimethyl-ammonium chloride (PDADMAC). This system has been applied to immobilize enzyme, microorganisms, animal cells and insect cells^[8–11]. This system exhibits good biocompatibility for biomass, stable chemical and physical properties, as well as with its preferable mechanical stability and appropriate mass transfer behavior^[8,9,11].

In this microcapsule system, NaCS is an important material which is derived by the sulfation of insoluble cellulose. The degree of polymerization (DP) of cotton cellulose is usually 300–1500^[12]. The relative molecular mass of NaCS is dependent not only on the DP of cellulose but also on the degree of substitution (DS) of cellulose sulfate. The monomer of cellulose (glucose) contains three OH-groups on C_2 -, C_3 - and C_6 -positions. According to the results of Wagenknecht^[13], the sulfation takes place generally ($DS < 1$) only on the C_6 -position.

Up to date, there are several processes for the preparation of cellulose sulfate, for example, homogeneous reaction process with the solution of $\text{DMF}\cdot\text{N}_2\text{O}_4$ and $\text{DMF}\cdot\text{SO}_3$ ^[14], heterogeneous reaction process with the solution of alcohol-sulfuric acid^[15,16] and with Me_3SiCl (chlorotrimethylsilane) and $\text{DMF}\cdot\text{ClSO}_3\text{H}$ (or SO_3)^[13], and others^[17,18]. NaCS produced by the process with alcohol-sulfuric acid is the only one that can be used as an encapsulation material. Its structure is shown in Fig.1(a). NaCS as a polyanion is able to form a 30–100 μm thick porous membrane with PDADMAC(polycation). The structure of PDADMAC is shown in Fig.1(b). The performance of the membrane is related to the properties of the two materials and the operation conditions in the encapsulation. PDADMAC, whose DP is 100–300(without DS), is relatively constant in its construction. But the properties of NaCS is strongly dependent on the production condition.

The sulfation of cellulose is the most important step in the preparation of NaCS and is a non-catalytic solid/fluid reaction. The kinetics of non-catalytic solid/fluid reaction for simple systems(i.e. gas/solid particle-reaction) has been described by Levenspiel^[19] with “progressive-conversion” model and the “unreacted-core” model. But for the system of natural polymer materials, related models are unavailable in any publications. This paper will try to examine

Received 1997-12-04, accepted 1998-05-04.

* Supported by the National Natural Science Foundation of China(No.29676069).

the reaction (sulfation) kinetics in the preparation of NaCS from cotton linter cellulose (linters) reacted with *n*-propanol and H₂SO₄.

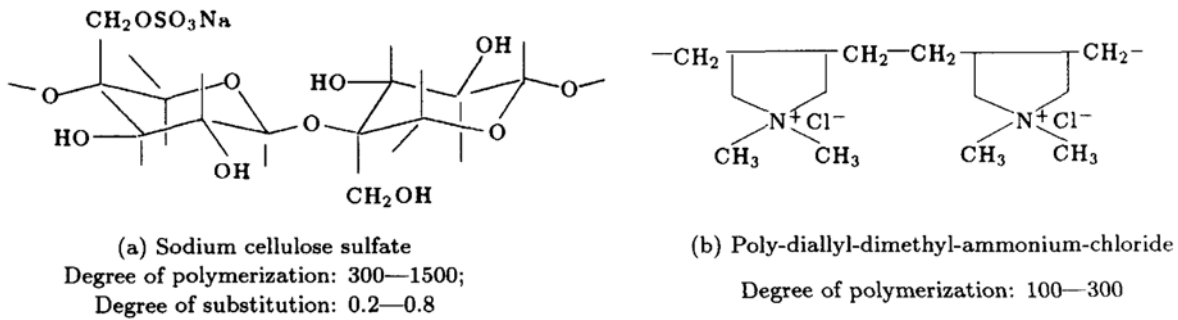
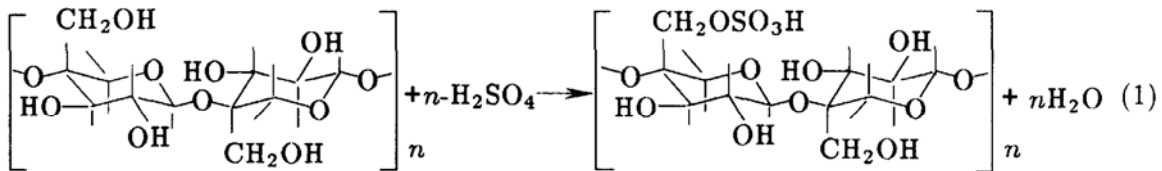


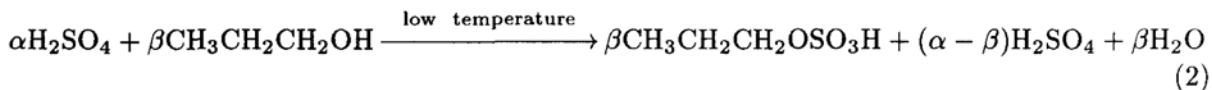
Figure 1 Structures of NaCS and PDADMAC

2 THEORETICAL AND KINETIC MODEL

The sulfation carried out in following form



It should be noted that neither H₂SO₄ diluted with water nor pure H₂SO₄ can be used, because the undesirable reactions such as hydrolysis and carbonization will occur and affect the sulfation. The solution used in our work is a mixture of *n*-propanol and H₂SO₄, reacting as follows



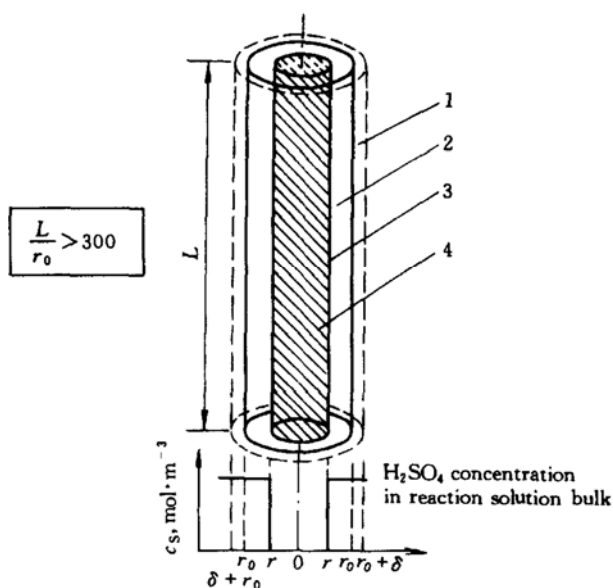
Therefore the kinetics of reaction (1) can be described in the following equations

$$-R_S = -1/nR_c \quad (3)$$

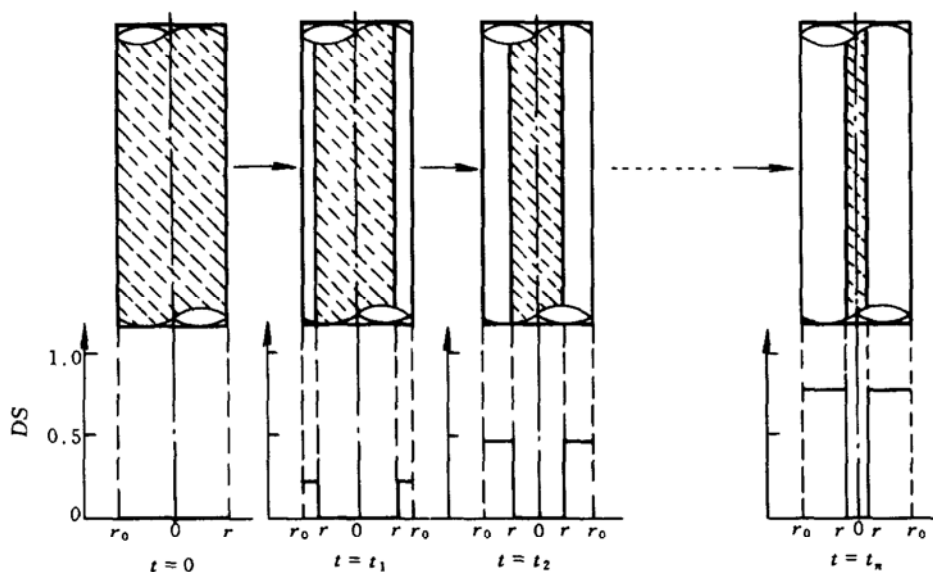
$$-R_S = k_S c_S^m \quad (4)$$

$$-R_c = -\frac{1}{A} \frac{dN_c}{dt} \quad (5)$$

The geometry of cellulose fiber can be assumed as cylinder. Fig.2(a) shows the assumed model of a fiber. Because the length of the cellulose fiber *L* is much greater than its diameter, the fiber can be considered as a infinitely long cylinder. Therefore the areas at the two ends of the fiber may be neglected and *L* can be assumed as a constant. The possible process of cellulose sulfation can be described as follows: The reaction takes place at first on the surface of cellulose fiber, until a layer of cellulose sulfate with increasing *DS* [as shown in Fig.2(b)] is formed; then, a reaction goes on from the outside to the inside, by which the *DS* in cellulose sulfate increases with time.



(a) Cellulose fiber taken to be cylindrical in form
1—liquid film, 2—product layer, 3—reaction surface, 4—unreacted core



(b) DS increasing with reaction time

Figure 2 Kinetic model for cellulose sulfation

The whole reaction process can be classified into three steps according to the theory of mass transfer and reaction:

(1) Diffusion of H_2SO_4 through the liquid film circulating around the cellulose fiber onto the surface of the fiber,

$$-R_{S,1} = k_{a,1}(c_{S,F} - c_{S,P}) \quad (6)$$

where $k_{a,1}$ is the mass transfer coefficient ($= D_F/\delta_F$, where D_F is the diffusion coefficient of H_2SO_4 in the liquid film, δ_F is the thickness of the film), $C_{S,F}$ and $C_{S,P}$ are the concentrations of H_2SO_4 in the liquid film and on the product layer, respectively.

(2) Diffusion of H_2SO_4 through the product layer to the reaction surface,

$$-R_{S,2} = k_{a,2}(c_{s,p} - c_{s,r}) \quad (7)$$

where $k_{a,2}$ is the mass transfer coefficient (D_P/δ_P , where D_P is the diffusion coefficient of H_2SO_4 in the product layer, δ_P is the thickness of the product layer), $c_{s,r}$ is the concentration of H_2SO_4 on the reaction surface.

(3) Reaction between H_2SO_4 and cellulose on the reaction surface and also in the product layer,

$$-R_{s,3} = k_s c_{s,r}^m \quad (8)$$

The total reaction rate is limited by the slowest step. Because the liquid film is very thin, the transfer resistance in this film is negligible. The resistance in the product layer can also be neglected due to the following reasons:

(1) According to the theory on gas/solid-catalytic reaction, the internal diffusion in the catalyst is negligible if the catalyst particle is very small. The cellulose fiber is very thin (the diameter is 8–32 μm) and the thickness of product layer is even much thinner, therefore the resistance of mass transfer in cellulose fiber can be totally neglected.

(2) It is well known that compared with mass transfer, reactive rate is far more sensitive to temperature. Some sulfation is considered at low temperature (-5 – $5^\circ C$), more slowing down in reactive rate is resulted, whereas mass transfer is not affected to such an evident. It follows then the reaction step will have to be the controlling step, thus, the total reaction rate may be expressed as

$$-R_c = -\frac{1}{A} \frac{dN_c}{dt} = -nR_{s,3} = nk_s c_{s,r}^m$$

when the H_2SO_4 concentration in the bulks is the same as that of reaction surface, i.e., $c_s = c_{s,p} = c_{s,r}$, then

$$-\frac{1}{A} \frac{dN_c}{dt} = nk_s c_s^m \quad (9)$$

where

$$A = 2\pi r L \quad (10)$$

$$N_c = \rho_c V c = \rho_c \pi r^2 L + \rho_c \pi L (r_0^2 - r^2) (1 - DS) \quad (11)$$

Since the DS of the product varies with time, Eq.(9) becomes

$$-\frac{1}{A} \frac{dN_c}{dt} = -\rho_c DS \frac{dr}{dr} + \frac{\rho_c (r_0^2 - r^2)}{2r} \frac{dDS}{dt} \quad (12)$$

and the differential equation for the sulfation kinetics is

$$\frac{(r_0^2 - r^2)}{2r} \frac{dDS}{dt} - DS \frac{dr}{dt} = K_S c_s^m \quad (13)$$

where $K_S = nk_s/\rho_c$. The first term on the left-hand side represents the sulfation resulted from DS in the product layer and the second term the sulfation due to the shrinking of the unreacted cellulose core.

The apparent conversion ratio of cellulose X can be measured, so that an equation of X as a function of the diameter of cellulose fiber can be represented as follows

$$X = (M_{c0} - M_c)/M_{c0} = (r_0^2 - r^2)/r_0^2 \quad (14)$$

$$r = r_0 \sqrt{1 - X} \quad (15)$$

where M_{c0} and M_c are the quantities of cellulose [g], r_0 and r are the radii of cellulose fiber at $t = 0$ and $t = t$, respectively.

$$\frac{dr}{dt} = -\frac{r_0^2}{2r} \frac{dX}{dt} \quad (16)$$

substituting Eq.(15) and Eq.(16) into Eq.(13),

$$\frac{1}{\sqrt{1 - X}} \left(DS \frac{dX}{dt} + X \frac{dDS}{dt} \right) = \frac{2K_s c_s^m}{r_0} \quad (17)$$

Eq.(17) can be readily solved when DS is constant or linearly related to time. For $DS = 1$, Eq.(17) becomes similar to the Levenspiel's model^[19]. If the following equation is satisfied,

$$DS = a + bt \quad (18)$$

And from Eq.(17),

$$\frac{dX}{K\sqrt{1 - X} - bX} = \frac{dt}{a + bt} \quad (19)$$

where

$$K = 2K_s c_s^m / r_0 = 2nk_s c_s^m / r_0 \rho_c \quad (20)$$

Integrating Eq.(19) at the condition of t [0, t] and X [0, X], the kinetic equation is obtained

$$\frac{K}{b\sqrt{(K/b)^2 + 4}} \ln \left[\frac{(\sqrt{(K/b)^2 + 4} + 2\sqrt{1 - X} + K/b)(\sqrt{(K/b)^2 + 4} - 2 - K/b)}{(\sqrt{(K/b)^2 + 4} + 2 + K/b)(\sqrt{(K/b)^2 + 4} - 2\sqrt{1 - X} - K/b)} \right] + \ln(\sqrt{1 - X} - bX/K) = -\ln[1 + (b/a)t] \quad (21)$$

Employing Eq.(21) the K -values at different c_s and T can be determined with the experimental data of X - t . Furthermore the relationship of the kinetic constant with T and the order of reaction m can be calculated.

3 MATERIALS AND EXPERIMENTAL

3.1 Materials

Cellulose: cotton linter cellulose, $DP = 1400$.

H_2SO_4 : CP, 95%—97%.

n -Propanol: analytical pure, 99%.

3.2 Apparatus

The apparatus for determining the conversion ratio of cellulose at different sulfation conditions is shown in Fig.3. The 25 ml reactor was jacketed with a cooling element for temperature control, and a glass filter was installed at the bottom of reactor.

3.3 Experimental

2 g (M_{c0}) cotton linters was packed into the reactor. The desired temperature was maintained by using the cooling bath. The reaction solution in the storage vessel was also kept at the desired temperature. The sulfation was started by the addition of reaction solution to the reactor. The mass flow rate of the solution was usually controlled at $5 \text{ g} \cdot \text{min}^{-1}$. At the defined reaction time,

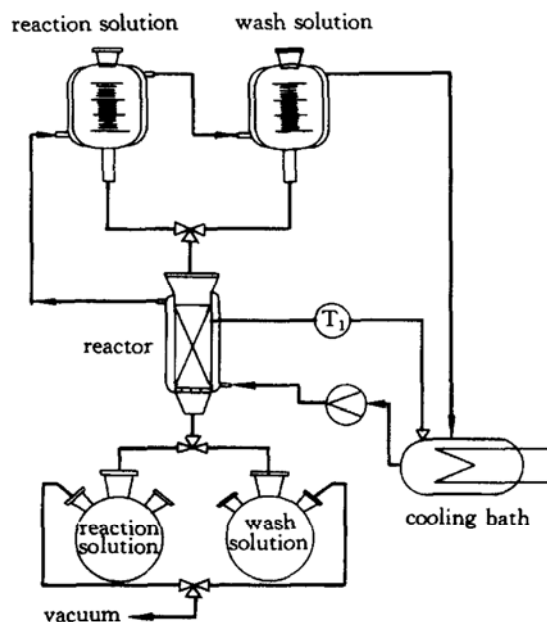


Figure 3 Apparatus for measurement of cellulose sulfation kinetics

the reaction solution was drawn out from the reactor. The solid mixture remaining in the reactor was cleaned with the wash solution. Thus mixture of cellulose sulfate/cellulose was then taken out from the reactor, and dissolved in water. Cellulose sulfate was soluble in water and unreacted cellulose was insoluble and was collected by filtration. The insoluble mass (unreacted cellulose) was rinsed for several times with water, and then dried at 105 °C. The dried weight was the amount of unreacted cellulose (M_c).

4 RESULTS AND DISCUSSION

4.1 Degree of substitution

Here DS is measured by using poly-electrolyte titration^[20], by which the amount of NaCS is determined by the titration quantity of PDADMAC.

The DS of NaCS varies with the sulfation condition. Normally, DS will increase with increases in reaction time, as well as temperature and H_2SO_4 concentration. Fig.4 shows these results. The data of DS can be regressed to relate reaction time, temperature and H_2SO_4 concentration [Eq.(22)]:

$$a = 5.433 \times 10^{-2} + 3.666 \times 10^{-4}(T - 273.15) + [-0.1074 + 4.575 \times 10^{-4}(T - 273.15)]c_s$$

$$b = -3.167 \times 10^{-3} + 1.092 \times 10^{-5}(T - 273.15) + [-3,599 \times 10^{-3} + 1.472 \times 10^{-5}(T - 273.15)]c_s \quad (22)$$

The results calculated by Eq.(22) are also given in Fig.4 shown in straight line.

4.2 Conversion ratio of cellulose

In Eq.(21) K is represented by

$$K = K_S c_S^m = K_S^0 \exp\left(-\frac{E}{RT}\right) c_S^m \quad (23)$$

The conversion ratios of cellulose X at different T and c_S are shown in Fig.5. The range of T is 268.15—278.15 K and that of c_S is 3.1—4.5 mol·L⁻¹.

With the experimental data, the values of K at different T and c_s can be calculated by the method of the nonlinear smallest square, so that constant K_s^0 , activation energy E and the order of reaction m can be determined

$$K = 2.516 \times 10^{10} \exp\left(-\frac{7.739 \times 10^4}{RT}\right) c_s^3 \quad (24)$$

The results show that the cellulose sulfation is a 3rd-order reaction related to c_s . The conversion ratios X at different T , c_s are calculated with Eq.(21) and Eq.(24). The calculated results are presented in Fig.5. The average relative error from 144 experimental data for X is 10.3%.

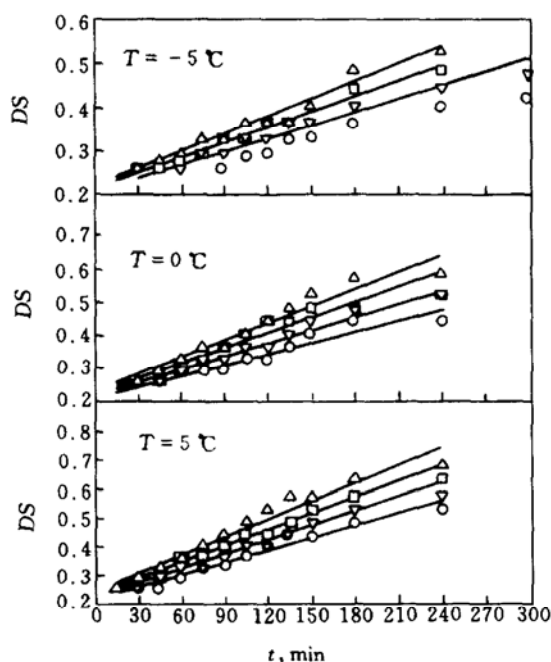


Figure 4 Variation of DS with sulfation conditions
 $\circ \nabla \square \triangle$ experimental data; — calculated values
 $c_s, \text{mol}\cdot\text{L}^{-1}$: \circ 3.105; ∇ 3.594; \square 4.052; \triangle 4.481

4.3 Yield of NaCS

The yield of NaCS Y is also dependent on the reaction conditions. It is defined as follows

$$Y = M_{\text{NaCS}}/M_{c0} \quad (25)$$

The mass of NaCS M_{NaCS} can be determined from X and DS

$$\begin{aligned} M_{\text{NaCS}} &= \frac{264(M_{c0} - M_c)DS + 162(M_{c0} - M_c)(1 - DS)}{162} \\ &= (M_{c0} - M_c)(1 + 0.6296DS) \end{aligned} \quad (26)$$

where 162 is the relative molecular mass of monomer of cellulose and 264 is that of the monomer of NaCS, so that Y is described as follows

$$Y = M_{\text{NaCS}}/M_{c0} = (1 + 0.6296DS)X \quad (27)$$

Therefore the Y values under different reaction conditions can be predicted with the experimental data of X and DS in Eq.(27). Fig.6 shows these results. And, with the calculated data of X [Eq.(21) and (24)] and DS [Eq.(22)], the yield Y_{cal} can also be predicted. The calculated results, which are shown in Fig.6, agree well with the true Y_{exp} . The average relative error of 144 points is 10.5%.

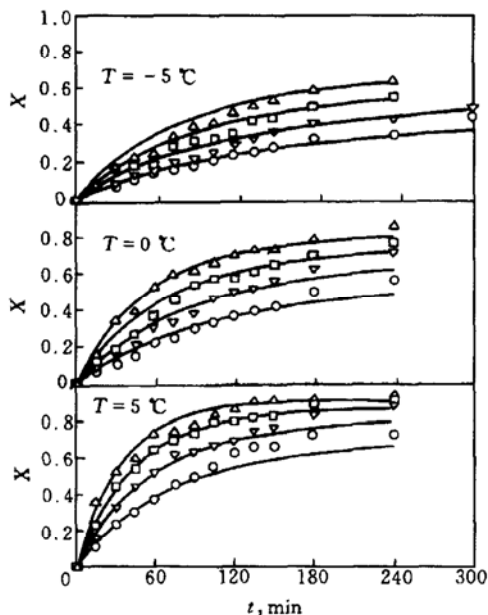


Figure 5 Comparison of experimental data with calculated values of cellulose conversion ratio

○ ▽ □ △ experimental data; — calculated values
 c_s , mol·L⁻¹: ○ 3.105; ▽ 3.594; □ 4.052; △ 4.481

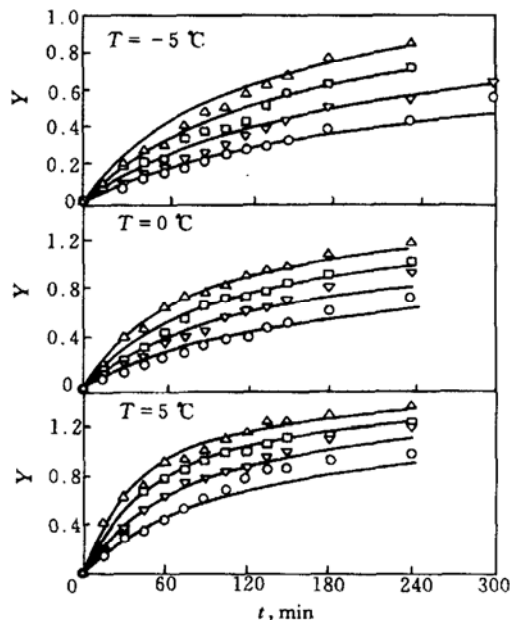


Figure 6 Comparison of experimental data with calculated values for yield of NaCS

○ ▽ □ △ experimental data; — calculated values
 c_s , mol·L⁻¹: ○ 3.105; ▽ 3.594; □ 4.052; △ 4.481

5 CONCLUSIONS

The kinetics of a system composed of a natural polymer material and a liquid medium is known to be very complex, though any knowledge in this respect will be most useful for process design. It is found that in the process of the preparation of sodium cellulose sulfate, the conversion ratio of cellulose and yield of cellulose sulfate are two important factors, whereas DS is an important property of the resultant NaCS for its encapsulation behaviour. If these variables could be relatively accurate, it will most possibly be of help in promoting product quality and be most useful in process design.

With certain appropriate assumptions, a kinetic model for the NaCS system has been established. With the proposed model, conversion ratio(X), NaCS yield(Y) and the degree of substitution(DS) may be predicted for the system within a comparatively wide range of reaction conditions. Relative good results should be expected. The proposed model will be very useful for scaling-up in process design.

ACKNOWLEDGEMENTS

The author wishes to acknowledge the support of Prof. Dr. R. Buchholz of his advice in this work.

NOMENCLATURE

A	surface area, m^2
c_S	H_2SO_4 concentration in the bulk, $mol \cdot m^{-3}$
$c_{S,F}$	H_2SO_4 concentration in the liquid film, $mol \cdot m^{-3}$
$c_{S,P}$	H_2SO_4 concentration on the surface of the fiber, $mol \cdot m^{-3}$
$c_{S,r}$	H_2SO_4 concentration on the surface of reaction, $mol \cdot m^{-3}$
D_F	diffusion coefficient of H_2SO_4 in the liquid film, $m^2 \cdot s^{-1}$
D_P	diffusion coefficient of H_2SO_4 in the product layer, $m^2 \cdot s^{-1}$
DP	degree of polymerization
DS	degree of substitution
E	activation energy, $J \cdot mol^{-1}$
K_S^0	constant in Eq.(23)
$k_{a,1}$	mass transfer coefficient in the liquid film, $m \cdot s^{-1}$
$k_{a,2}$	mass transfer coefficient in product layer, $m \cdot s^{-1}$
k_S	kinetic constant, $mol^{1-m} \cdot m^{3m-2} \cdot s^{-1}$
m	the order of reaction
N_c	amount of substance of cellulose, mol
n	stoichiometric coefficient for cellulose sulfation
R	molar gas constant, $J \cdot mol^{-1} \cdot K^{-1}$
R_c	reaction rate of cellulose, $mol \cdot m^{-2} \cdot s^{-1}$
R_S	reaction rate of H_2SO_4 , $mol \cdot m^{-2} \cdot s^{-1}$
T	temperature, K
t	reaction time, s
δ_F	thickness of the film, m
δ_P	thickness of the product layer, m
ρ_c	cellulose molar density, $mol \cdot m^{-3}$

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