WASTEWATER TREATMENT -

PHENOL EXTRACTION BY LIQUID MEMBRANE

BY

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APPROVAL SHEET

Title of Thesis : Wastewater Treatment - Phenol Extraction

by Liquid Membrane

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ABSTRACT

Title of Thesis : Wastewater Treatment -

                    Phenol Extraction by Liquid Membrane

Jan-Ming Hou, Master of Science, 1988

Thesis directed by : Dr. Ching-Rong Huang

Two models for the extraction of phenol by means of
liquid surfactant membranes is presented in which external
mass transfer around W/O emulsion drop, phase and chemical
equilibria are taken into account.

The nonlinear coupled P.D.E.'s is solved under
assumptions to get a close-formed analytical approximate
solution. The experimental results on the batch extraction
of phenol are found to be satisfactory simulated by
one of the proposed models provided that phenol
concentration is higher than 0.01N. The model requires no
adjustable parameter thus it can predict the extraction
behavior without doing experiments.

ACKNOWLEDGEMENT

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I. Introduction and Literature Review

The introduction of liquid membrane separation technique in industrial application was first made by Li (Li, 1968) almost two decades ago. Since then, numerous investigations have been made concerning the area of applications, the separation processes, the physical and chemical natures and theoretical modelling of this novel separation technique.

Liquid membrane separation has demonstrated considerable potential as effective tools for an increasingly wide variety of applications. Such as

1. the organic compounds separation (Li, 1968; 1971a, 1971b; Shah and Owens, 1972; Cahn and Li, 1976a, 1976b; Alessi et., 1980; Halwachs et al., 1980; Terry et al., 1981);

2. the recovery and enrichment of heavy metal ions (Schiffer et al., 1974; Hochhauser and Cussler, 1975; Martin and Davies, 1976/1977; Kondo et al., 1979; Volkel et al., 1980; Strzelbicki and Charewicz, 1980; Frankerfeld et al., 1981);

3. the treatment of wastewater (Li and Shrier, 1972; Cahn and Li, 1974; Frankfeld and Li, 1977; Kitagawa et al., 1977; Halwachs et al., 1980; Terry et al., 1981);

4. the application in biochemical and biomedical fields (May and Li, 1972; Li and Asher, 1973; May and Li, 1974; Mohan and Li, 1974, 1975; Asher et al., 1975, 1977; May and Li, 1977; Frankenfeld et al., 1978);

Also, liquid membrane separation showed potential utility as

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5. membrane reactors in cooperating simultaneous separation and reaction process (Ollis et al., 1972; Wylynic and Ollis, 1974; Cussler and Evans, 1980).

As respect to mechanism, there are two types of liquid membrane systems as identified by Matulevicius and Li (1975) and Li (1978, 1981), so called type I and type II mechanism. They all have the same basic principles, namely, a liquid membrane phase and the receiving phase (usually both are aqueous solutions) were separated by the membrane, an organic solution. Because of the immiscibility of the organic solvent and aqueous solution, the source and receiving phases were set apart with stability. The extractant, in the source phase, will be extracted into the membrane phase and then the receiving phase.

One way to increase the yield of extraction is to add some kind of chemicals in the receiving phase which could react with the extractant irreversibly. This type of facilitation is the type I mechanism.

Another way to achieve this goal is to use so called "carrier" in the membrane phase. It is soluble in the organic solvent but not in water. It serves as a "shuttle bus", moving toward the source phase/membrane phase interface and reacting with the extractant to form complex, the complex will diffuse toward the membrane phase/receiving phase and release the extractant to the receiving phase. This type of

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transport - complex toward the receiving phase and carrier toward the source phase (but both are confined within the membrane phase) - is the basic mechanism for type II facilitation.

If we consider the physical constructions, there are also two types of liquid membrane systems. The first one is called the supported liquid membrane system. In such system, the membrane is formed by absorbing a suitable membrane solvent into a microporous solid film. The second one is called the emulsified liquid membrane system, in brief ELMS, which is the focus of the present work and worth while to discuss in more detail.

The whole operating process is illustrated in Fig. 1.1-1 The process can be divided into two steps: 1. the emulsion preparation step and the mixing of membrane phase (organic solvent) and internal aqueous phase (aqueous solution) in high shear emulsification (1,000rpm). After this step, the receiving mixture is then mixed with the external aqueous phase under a low stirring speed, during this CSTR operation, the extractant in external aqueous phase is extracted into the internal aqueous phase. The detail mechanism will be discussed in next chapter.

Since 1970's, many mathematical models were proposed attempting to adequately describe the ELMS systems. Six types of models have been proposed.

oil phase

aqueous receiving phase

rapid mixing →

two phase emulsion

addition to agitated external source phase

external source phase

emulsion & source phase separation

emulsion phase breaking

emulsion phase

recovered membrane phase

return to process

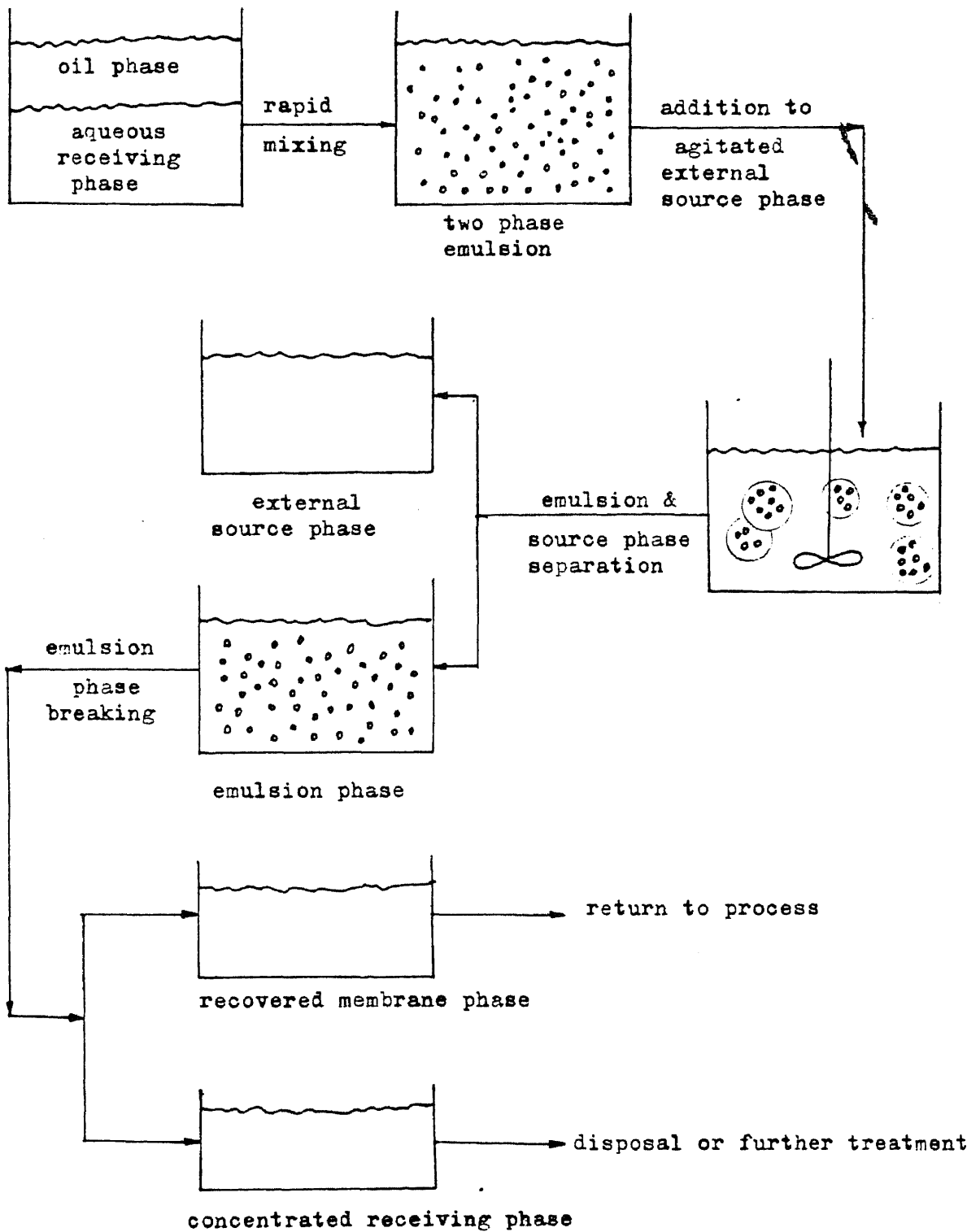concentrated receiving phase

disposal or further treatment

Fig 1.1-1 Sequences of liquid membrane separation process

(1) Uniform flat – sheet model (Cahn and Li, 1974)

(2) Hollow sphere model (Matulevicius and Li, 1975)

(3) Hollow sphere – advancing front model

(4) Immobilized globule – advancing front model (Ho et al, 1982)

(5) Immobilized hollow spherical globule – advancing front model (Kim et al, 1983)

(6) Immobilized globule – diffusion with reaction model (Teramoto et al, 1983)

The uniform flat – sheet model assumes that all of the fine droplets within the emulsion are coalesced into a single large droplet, and the mass transfer process consists of diffusion across a stagnant membrane of thickness. Furthermore, the membrane thickness is assumed to be negligible compared to the drop radius, so it can be considered as uniform flat membrane thickness.

The hollow – sphere model (model 2) made a modification of Model (1) by considering the spherical geometry of the emulsion globule. Model (3) is basically the same as the hollow sphere model except that all of the fine droplets within the emulsion are coalesced into a single large droplet, and this droplet is encapsulated in a stagnant hollow spherical membrane film. However, the internal reagent phase in this model is assumed to be immobilized and the solute reacts irreversibly with the reagent at a reaction surface which advances into the droplet center while the reagent is

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being consumed. Model (4) uses the advancing front idea, but more realistically assuming the heterogenity of the internal droplets. Model (5) has the same idea, but including a perispherical membrane film. The idea of advancing front is really not that convincing, because inside the globule, internal droplets are discontinuously distributed. Model (6) took this factor into account. It is assumed that spherical shell within the globule, the extraction, with or without reaction, occurs in the internal droplets, but outside the droplet, where the membrane phase is, diffusion occurs. Model (6) is chemico-physically the most comprehensive model, but because the complexity of the internal reaction, all solutions, based on the idea of model (6), use numerical techniques. This created a problem when applying the model for batch operation to CSTR operation. Also, some physical parameters, such as external mass transfer coefficient and difficulty are treated as adjustable variables in order to fit the experimental results (Teramoto, 1981, 1983).

Wang, basing chemical equilibrium assumption, solved model (6) and got an analytic solution. But the solution failed to predict the effect of some operational parameters, such as the external phase concentration and the internal chemical reagent concentration.

The purpose of this research is to develop a mathematical model, for type I facilitated ELMS, which can be solved analytically, and can predict the behavior of the

system while changing the operating conditions.

II. Theory and Mathematical Model

2.1 Theory

Type I facilitated liquid membrane extraction can be demonstrated by, for example, phenol extraction. As shown in Fig. 2.1-1, the elementary mechanism of phenol permeation through the liquid membrane are as follows:

(1) The phenol diffuses through the stagnant film of the external aqueous phase.

(2) The phenol is absorbed from external aqueous phase to membrane phase.

(3) The phenol, in membrane phase, diffuses from the external phase/membrane phase interface toward the core of the globule.

(4) When phenol encounters the internal aqueous phase, while diffusing through the membrane, the phenol will react with the internal chemical species, such as sodium hydroxide, giving an end product sodium phenoxide. This can keep the phenol concentration low in the internal phase because of the highly favored forward reaction.

To make this very complicated problem managable, several assumptions were made:

(1) Globules size variations can be lumped into a single effective mean diamer.

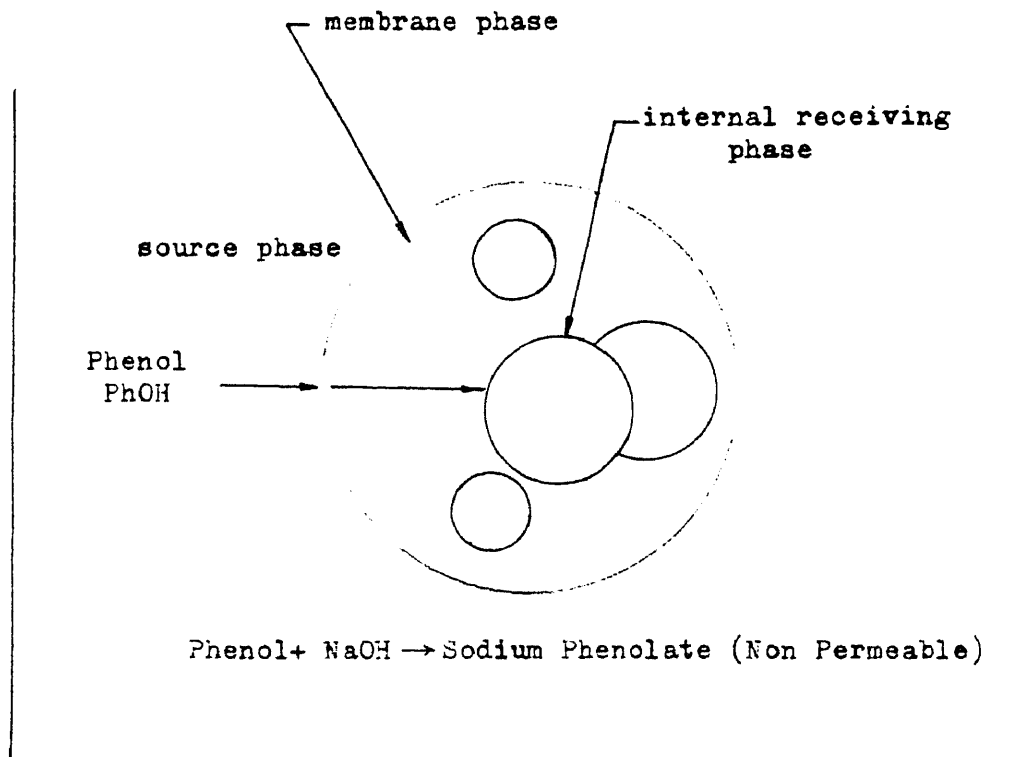(2) Mass transfer within the globules is diffusion control.

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Fig 2.1-1 Mechanism of phenol removal with liquid membranes

(3) No internal circulation occurs within the globule.

(4) Membrane breakage is neglected.

(5) Coalescense and redispersion of globules are negligible.

(6) The system is well-agitated, so the external aqueous phase concentration is a function of time only.

(7) Local phase equilibrium holds between membrane and aqueous phases.

(8) The concentration within the internal phase droplets are uniform.

(9) The volume change of the globules are negligible.

(10) The reaction product is confined within the internal droplets.

(11) Chemical equilibrium applies throughout the globules.

A few additional comments are warranted. Assumption (1) removes the complication caused by globule size distribution. Teramoto et al. (1986) compared the results of two models, one of which used the Sauter mean diameter as the average diameter of the drops, the other one took the globule size distribution into consideration. These two models give very close results which implies that the assumption (1) is very good.

The importance of the external mass transfer resistance has been demonstrated by several authors (Kim, 1983; Teramoto, 1983, 1981; Steiner, 1986; Fales, 1984).

2.2 Mass Transfer Model - Basic Equations

Based on the proceeding mechanism and assumptions, the diffusion equation in the membrane phase is

$$(1 - e) \frac{\partial C_m}{\partial t} = D_{eff} \cdot \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C_m}{\partial r} \right) \right] - Rx$$

$$(2.2-1)$$

The initial and boundary conditions are

1.c.   at $t = 0$ $C_m = 0$ for $0 < r < R$ (2.2-2)

B.C.1   at $r = 0$ $C_m =$ finite   (2.2-3)

B.C.2   at $r = R$ $C_m = C_m = a_e C_e$ (2.2-4)

Where C: phenol concentration

D_{eff} : effective dissusivity

e: volume fraction of internal phase in the emulsion

globule

$$(e = \frac{V_i}{V_i + V_m})$$

V: volume

R: Sauder's radius of emulsion globules

a: phase equilibrium constant

Rx: rate of phenol reacted per unit volume of emul-

sion globule

Subscripts

e: external phase

m: membrne phase

i: internal phase

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superscript

': phase equilibrium

The mass balance on external phase leads to the following equation :

$$V (1 - f) \frac{dC_e}{dt} = - N (4\pi R^2) D_{eff} \cdot (\frac{\partial C_m}{\partial r})_{r=R}$$

(2.3-5)

with initial condition

at t = 0 $C_e = C_o$ (2.3-6)

Where $V = V_i + V_e + V_m$

$$f = \frac{V_i + V_m}{V}$$

N: the total number of emulsion globules

Subscript

o: initial state

Because $N = \frac{V \times f}{4/3\pi R^3}$, equation (5) can be written as

$$\frac{dC_e}{dt} = - \frac{3 \cdot f}{1 - f} \frac{D_{eff}}{R} (\frac{\partial C_m}{\partial r})_{r=R}$$

(2.2-7)

Further, since the film resistance is considered, then

$$k \cdot (C_e - C_e) = D_{eff} \cdot (\frac{\partial C_m}{\partial r})_{r=R}$$

(2.2-8)

where

k: mass transfer coefficient

While phenol is extracted from membrane into the internal droplets, it will either be reacted to form sodium phenoxide or just stay as it is. So, we can write

$$Rx = e \left(\frac{\partial C_{Pi}}{\partial t} + \frac{\partial C_i}{\partial t} \right) \qquad (2.2-9)$$

Where C_{Pi} is the concentration of sodium phenoxide in the internal droplets.

2.3 Mass Transfer Model - Case I

In this case, it is assumed that phenol in the membrane phase reacts with the sodium hydroxide in the internal phase and reaches equilibrium at any time and place. That is

$$A_m + B_i \rightleftharpoons P_i$$
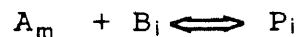
Where A denotes for phenol, B for sodium hydroxide and P for sodium phenoxide. The subscript m indicates membrane phase, and i internal phase.

Since equilibrium is reached everywhere at any time, so

$$K = \frac{C_{Pi}}{C_{Am} \times C_{Bi}} \qquad (2.3-1)$$

The mass conservation law insures that

$$C_{Bo} = C_{Bi} + C_{Pi} \qquad (2.3-2)$$

Where subscript o means initial condition.

But, in pratical application, C_{Bi} is much larger than C_{Pi}

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which gives

$$C_{Bi} \approx C_{Bo} \qquad\qquad (2.3-3)$$

Substituting equations (2.3-3) into equation (2.3-1) results in

$$K = \frac{C_{Pi}}{C_{Am} \times C_{Bo}}$$

or

$$C_{Pi} = K \times C_{Bo} \times C_{Am} = constant \times C_{Am} \quad (2.3-4)$$

Further, assuming that phase equilibrium exists, i.e.

$$C_{Ai} = a_i \cdot C_{Am} \qquad\qquad (2.3-5)$$

Where a is the phase equilibrium constant. Combining eq. (2.3-5) and (2.2-9) gives

$$Rx = e \times (a_i + KC_{eo}) \frac{\partial C_{Am}}{\partial t} \qquad (2.3-6)$$

Let $q = a_i + KC_{Bo}$ and note that C_{Am} is just a different notation for C_m then

$$Rx = e \times q \times \frac{\partial C_m}{\partial t} \qquad\qquad (2.3-7)$$

Putting eq. (2.3-7) into eq. (2.2-1), and using following dimensionless variables

$$K_1 = \frac{3 f}{1 - f}$$

$$K_2 = 1 - e + q e$$

$$r = r/R$$

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$$t = \frac{D_{eff}}{R^2} t$$

$$Bi = \frac{R \times k_e}{a_e \times D_{eff}}$$

$$g = a_e C_m / C_{eo}$$

and

$$h = C_e / C_{eo}$$

will change equations (2.2-1) to (2.2-5), and (2.2-7) to (2.2-8) into dimensionless form.

$$\frac{\partial g}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial g}{\partial r} \right) \qquad (2.3-8)$$

I.C. $t = 0$ $g = 0$ (2.3-9)

B.C.1 $r = 0$ g is finite   (2.3-10)

B.C.2 $r = 1$ $h' = g'$ (2.3-11)

$$\frac{dh}{dt} = - Bi \, (h - h') \qquad (2.3-12)$$

I.C. $t = 0$ $h = 1$ (2.3-13)

$$Bi \, (h - h') = \left(- \frac{\partial g}{\partial r} \right)_{r=1} \qquad (2.3-14)$$

These set of equations are linear equations and can be solved by method like Laplace Transform. The solutions are

$$h = C + \sum_{n=1}^{\infty} \frac{(Bi - 1) \tan b_n + b_n}{A_n} T_n$$

$$(2.3-15)$$

$$g = C + \sum_{n=1}^{\infty} \frac{Bi}{An} \, Tn \, \frac{Sin \, (bn \, r)}{r \, Cos \, bn} \qquad (2.3\text{-}16)$$

$$Tn = \exp\left(-\frac{bn^2 \cdot t}{K_2}\right) \qquad (2.2\text{-}17)$$

$$\tan bn = \frac{bn \cdot (K_1 K_2 Bi - bn^2)}{K_1 K_2 Bi + bn^2 (Bi - 1)} \qquad (2.3\text{-}18)$$

$$C = \frac{3}{3 + K_1 K_2} \qquad (2.3\text{-}19)$$

$$An = \left(Bi - 1 - \frac{bn^2}{2} + \frac{K_1 K_2 Bi}{2}\right) \tan bn$$

$$+ \left(\frac{Bi}{2} + 1\right) \qquad (2.3\text{-}20)$$

2.4 Mass Transfer Model - Case II

In this case, two-step-equilibrium mechanism is considered. First, phenol in the membrane phase is in equilibrium with that in the internal phase; then, in the internal droplet, chemical equilibrium holds. The following equations express this idea.

$$C_{Am} = a_i \, C_{Ai} \qquad (2.4\text{-}1)$$

$$A_i + B_i \rightleftharpoons P_i$$

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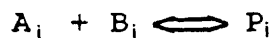
with equilibrium constantant

$$K = \frac{C_{Pi}}{C_{Ai} \cdot C_{Bi}} \qquad (2.4-2)$$

The basic difference between Case I and Case II is that in Case I, chemical equilibrium holds for phenol (A) in membrane phase, but in Case II, in the internal phase. In order to solve C_{Pi} in term of C_{Am}, another equation is required and can be provided by mass conservation law, i.e.

$$C_{Bo} = C_{Bi} + C_{Pi} \qquad (2.3-2)$$

From equations (4.2-1), (4.2-2) and (2.3-2), CPi can be solved as

$$C_{Pi} = \frac{K \cdot C_{Bo} C_{Am}}{1 + K \cdot C_{Am}} \qquad (2.4-3)$$

Comparing to equation (2.3-4), (2.3-5) and (2.3-6) provided that the change of C_{Am} is not very big a equation similar to eq. (2.3-7) can be obtained, i.e.

$$Rx = e\,q\, \frac{\partial C_m}{\partial t} \qquad (2.4-4)$$

where

$$q = \left(a_i + \frac{K \cdot C_{Bo}}{1 + K \cdot C_{Am}} \right) \qquad (2.4-5)$$

Since q is no longer a constant as it is in Case I discussed previously, it is impossible to solve the mass transfer model (Chapter 2.2) analytically.

To get an adequate solution without involving tedious computing routines in numerical analysis, a very simple computation algorithm is proposed.

From common physical and mathematical senses, solutions for Case I can at least qualitatively describe Case II. So if the solutions in Case I can be reasonably modified, we can use them as the approximate solutions for Case II. There is no rigid theory background to estimate the error, but this can be overcome by using experimental data compared to the approximate solutions to see the applicability.

To demonstrate this idea, equation (2.4) is changed to dimensionless form as in Chapter 2.3.

$$q = \left(1 + \frac{K_4}{1 + K_3 g} \right) \qquad (2.4\text{-}6)$$

where

$$K_3 = K \left(a_i / a_e \right) \times C_m \qquad (2.4\text{-}7)$$

$$K_4 = KC_{eo} \qquad (2.4\text{-}8)$$

It is assumed that equations (2.3-15) and (2.3-16) for Case I are applicable to Case II.

$$h = C + \sum_{n=1}^{\infty} \frac{(Bi - 1) \tan bn + bn}{An} Tn \qquad (2.3\text{-}15)$$

$$g = C + \sum_{n=1}^{\infty} \frac{Bi}{An} Tn \frac{Sin(bn\, r)}{r Cos\, bn} \qquad (2.3\text{-}16)$$

The definitions of variables in these equations are described in Chapter 2.3. The only difference now is that q is no longer a constant. It is necessary to find the proper value of q, and apply it to equation (2.3-15), but noted that q is a function of r and t.

From equation (2.3-5), it is known that in solving h, the value of q at r = R has to be known. has to have the value at r = R. With this understanding, the

following computing algorithm is proposed.

(1) let t = t1 the desired time,

(2) let r = R (= 1) and use equations (2.4-6) and (2.3-16) to find g and q.

(3) apply q in (2) to eq. (2.3-15) to find h at time t1

(4) let t = t2, repeat step 2 and 3, and so on ....

Following this procedure, h at different time can be easily computed.

III. Parameter Evaluation

3.1 Effective Diffusivity

The effective diffusivity D_{eff} of phenol in the emulsion mixtures based on the concentration driving force defining in terms of the membrane phase concerntration, C , can be estimated by using the Jefferson-Witzell-Sibbit equation for diffusion through a composite medium (Ho, 1982; crank, 1975) which, in our notation is

$$D_{eff} = D_m \left[\frac{4(1+2P)^2 - \pi}{4(1+2P)^2} \right] + \frac{\pi}{4(1+2P)} \left(\frac{D_A D_m}{D_A + 2PD_A} \right) \qquad (3.1-1)$$

where

$$D_A = \frac{2(D_i/a_i) D_m}{(D_i/a_i) - D_m} \left[\frac{D_i/a_i}{(D_i/a_i) - D_m} \ln \left(\frac{D_i/a}{D_m} \right) - 1 \right] \qquad (3.1-2)$$

$$P = 0.403 \left(\frac{V_i}{V_i + V_m} \right)^{-1/3} - 0.5 \qquad (3.1-3)$$

D_i and D_m are the diffusivities of phenol in membrane phase and internal phase respectively, which were estimated by Wilke-Chang correlation (Reid et al., 1977), following Ho et al.'s (1982) evaluation, for phenol in SI units

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$$D_i = 1.17 \times 10^{-16} \; \frac{T \, (W \, M)^{0.5}}{V_A^{0.6} \, \mu} \; m^2/s \quad (3.1\text{-}4)$$

W is the solvent dissociation factor, it is 2.6 for the aqueous phase and 1.0 for the oil phase. μ is the viscosity of solvent at the absolute temperature T. M is the molecular weight of the solvent and V_A is the molar volume of solute at normal boiling point. In type I facilitated liquid membrane transfer, there is reaction in the internal droplets, which will change the apparent diffusivity. This effect could be taken into account by modifying eq. (3-2) in the following way

$$D_A = \frac{2 \, (D_i \, q / a_i) \, D_m}{(D_i \, q / a_i) - D_m}$$

$$\times \left[\frac{D_i \, q / a_i}{D_i \, q / a_i - D_m} \ln \left(\frac{D_i \, q}{a_i \, D_m} \right) - 1 \right] \quad (3.1\text{-}5)$$

and

$$q = 1 + \frac{K C_{io}}{(1 + K \cdot C_{eo} \cdot g)} \quad (3.1\text{-}6)$$

obviously q is a function of g ($C_m / a_e C_{eo}$), and in equation (5), the average q is used, i.e. integrating over g from 0 to 1.

$$q = 1 + \frac{K C_{io}}{K \cdot C_{eo}} \left(1 - \frac{1}{1 + K \cdot C_{eo}} \right) \quad (3.1\text{-}7)$$

The computation procedure is illustrated by the following example.

Example 3.1-1 : Experimental conditions and physical parameters (Teramoto, 1983)

water : $M = 18$ kg / kg - mole

$\mu = 1.0 \times 10^{-3}$ N.S / m

$W = 2.6$

kerosene : $M \sim 180$ kg / kg - mole

(average molecular weight)

$\mu \sim 2.2 \times 10^{-3}$ N.S / m^2

(Perry's 4th ed)

$W = 1.0$

phenol : $V_A = 102 \times 10^{-3}$ m^3 / kg - mole

Equilibrium constant
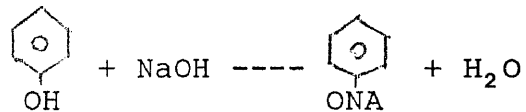
K = 1.1×10^4 (Morrison et al.,1966)

Partition coefficient

$a = 1.0$

Operating conditions

$V_i = 50$ ml

$V_m = 50$ ml

$C_{io} = 0.3$ N

$C_{eo} = 0.0212$ N

From eq. (3.1-4)

$$D_i = 1.17 \times 10^{-16} \; \frac{298 \, (\, 2.6 \times 18 \,)^{0.5}}{1 \times 10^{-3} \times (\, 102 \times 10^{-3} \,)^{0.6}}$$

$$= 9.38 \times 10^{-10} \; m^2/s$$

$$D_m = 1.17 \times 10^{-16} \frac{298 \, (\, 1.0 \times 180 \,)^{0.5}}{2.2 \times 10^{-3} \times (\, 102 \times 10^{-3} \,)^{0.6}}$$

$$= 8.34 \times 10^{-10} \; m^2/s$$

From eq. (3.1-3)

$$P = 0.403 \, (\, \frac{50}{50 + 50} \,)^{-1/3} \quad - 0.5$$

$$= 7.75 \times 10^{-3}$$

From eq. (3.1-7)

$$q = 1 + \frac{1.1 \times 10^4 \times 0.3}{1.1 \times 10^4 \times 1 \times 0.0212}$$

$$\times \, (\, 1 - \frac{1}{1.1 \times 10^4 \times 1 \times 0.0212} \,)$$

$$= 15.1$$

$$D_i \cdot q / a_i = 9.38 \times 10^{-10} \times 15.1 / 1 = 1.4 \times 10^{-8}$$

From eq. (3.1-5)

$$D_A = \frac{2 \, (\, 1.4 \times 10^{-8} \,) \, 8.34 \times 10^{-10}}{1.4 \times 10^{-8} - 8.34 \times 10^{-10}}$$

$$x \left[\cfrac{1.4 \times 10^{-8}}{1.4 \times 10^{-8} - 8.34 \times 10^{-10}} \right.$$

$$x \ln \left(\cfrac{1.4 \times 10^{-8}}{8.34 \times 10^{-8}} \right) - 1 \left. \right]$$

$$= 3.56 \times 10^{-10}$$

From eq. (3.1-1)

$$D_{eff} = 8.34 \times 10^{-10} \ x$$

$$\left[\cfrac{4 \ (\ 1 + 2 \times 7.75 \times 10^{-3} \ )^2 - \pi}{4 \ (\ 1 + 2 \times 7.75 \times 10^{-3} \ )^2} \right]$$

$$+ \cfrac{\pi}{4 \ (\ 1 + 2 \times 7.75 \times 10 \ )} \ x$$

$$\left[\cfrac{3.56 \times 10^{-9} \times 8.34 \times 10^{-10}}{8.34 \times 10^{-10} + 2 \times 7.75 \times 10^{-3} \times 3.56 \times 10^{-9}} \right]$$

$$= 27.8 \times 10^{-10} \ (m^2/s)$$

3.2 External Mass Transfer Coefficient k.

The two simplest cases of steady-state mass transfer are mass transfer to drops rigid in character and to those with fully developed internal circulation.

Most authors agree that the best correlation for the rigid drops is in the form of the following equation:

$$Sh_c = 2 + C_1 Re^{C_2} Sc^{C_3} \qquad (3.2-1)$$

$$Sh = 2 + 0.6 Re^{1/2} Sc^{1/3} \qquad (3.2-2)$$

Where C1, C2 and C3 are constants. The subscript C indicates external continuous phase. The exponent C3 of the Schmidt number is usually taken as 1/3, the one of the Reynolds number is 1/2. And C1 is ranging from 0.4 to 0.6. After investigating numerous binary systems, Steiner (1979) proposed an empiricial equation

$$Sh_{cr} = 2.43 + 0.775 Re^{1/2} Scc^{1/3}$$
$$+ 0.0103 ReSc^{1/3} \qquad (3.2-3)$$

The constant factor 2.4-3 may be replaced by its theoretical value of 2 on left out completely as its influence is low in the relavent region (i.e. medium Reynolds numbers between 10 and 1,000, Schmidt number around 1,200).

For prefectly circulating drops, i.e. when the surface velocity is identical to the circulating velocity of the continuous phase, the equation was originally developed by Bousinesg (1905), but it is sometimes called Higbie's equation, as it is easily derived from penetration theory. It may be written as

$$Sh_{ca} = (2/\Pi^{0.5})Re^{1/2} Sc^{1/2} \qquad (3.2-4)$$

For many binary system, the mass transfer is from imperfectly circulating drops. Here Steiner's correlation (1986) is used. The Peclet number is the product of the Reynolds and the Schmidt numbers. Shc is the resulting value for rigid (Sh_{cr}) and perfectly circulating drops (Sh_{ca}).

The range of data used in eq. (3.2-4) is for Re from 10 to

25

1,200, Sc from 190 to 241,000, which covers the full range of hydrodynamic conditions.

In computing Reynolds numbers, the terminal velocity of the globules has to be known. This is obtained by the following procesure.

First, the terminal velocity based on Stoke's law is computed through the following equation

$$V_{T.S.} = \frac{d_p^2 \ (\rho_c - \rho_p) \ g}{18 \ \mu_c} \qquad (3.2-6)$$

Where the subscript P indicates " partical ".
Then using this velocity, the Reynolds number can be caculated.

$$Re_{T.S.} = \frac{d_p \ V_{T.S.} \ \rho_c}{\mu_c}$$

$$= \frac{g d_p^3 \ \rho_c \ (\rho_c - \rho_p)}{18 \ \mu_c^2} \qquad (3.2-7)$$

From this Reynolds number and table 3.2-1, this ratio of terminal velocity to the terminal velocity based on Stoke's law is estimated.

Table 3.2-1

$Re_{T.S.}$	1	10	100	1,000	10,000	100,000
$V_T / V_{T.S.}$	0.9	0.65	0.37	0.17	0.07	0.023

Finally, the terminal velocity V is

$$V_T = \cfrac{V_T}{V_{T.S.}} \times V_{T.S.} \qquad\qquad (3.2-8)$$

The full procedures in estimating   is illustrated by the following example.

Example: Experimental conditions and physical parameters.

Membrane globuls.

50% kerosene + 50% water

ρ (kerosene) = 754 kg/m^3 (average density)

ρ (water) = 1,000 kg/m^3

ρ_p = 754 x 50% + 1,000 x 50%

= 877 kg/m^3

d_p = 0.152 cm = 1.52 x 10^{-3} m

continuous phase (water)

ρ_c = 1,000 kg/m

μ_c = 1.0 x 10^{-3} N.m/s^2

D_c = 9.38 x 10^{-10} m^2/s

gravitational accelaration

g = 9.8 m/s^2

From eq. (3.2-6)

$$V_{T.S.} = \cfrac{(1.52 \times 10^{-3})\ (1,000 - 877)\ 9.8}{18 \times 1.0 \times 10^{-3}}$$

$$= 0.155 \text{ m/s}$$

From eq. (3.2-7)

$$Re_{T.s.} = \frac{(1.52 \times 10^{-3}) (0.155) (1,000)}{1.0 \times 10^{-3}}$$

$$= 235.6$$

From table 3.1-1

$$\frac{V_T}{V_{T.s.}} = 0.3$$

From eq. (3.2-6)

$$V_T = 0.3 \times 0.155$$

$$= 0.0465 \text{ m/s}$$

$$Re = \frac{\rho_c \, d_p \, V_T}{\mu_c}$$

$$= \frac{1000 \times (1.52 \times 10 \quad) \times 0.0465}{1 \times 10}$$

$$= 70.68$$

$$Sc = \frac{\mu_c}{\rho_c \, D_c}$$

$$= \frac{1 \times 10^{-3}}{1,000 \times 9.38 \times 10^{-10}}$$

$$= 1,066$$

From eq. (3.2-2), taking C1 = 0.6, C2 = 0.5 and C3 = 1/3

$$Sh = 2 + 0.6 (70.68)^{1/2} (1,066)^{1/3}$$

$$= 53.53$$

$$\frac{k_o d_p}{D_c} = 53.53$$

$$k_o = \frac{9.38 \times 10^{-10} \times 70.68}{1.52 \times 10^{-3}}$$

$$= 4.36 \times 10^{-5} \ m/s$$

From eq. (3.2-4)

$$Sh_{ca} = \frac{2}{\pi^{0.5}} \ (\ 70.68 \ ) \ \cdot \ (\ 1,066 \ )$$
$$= 309.73$$

From eq. (3.2-5)

$$\frac{Sh_c - Sh_{cr}}{Sh_{ca} - Sh_{cr}} = 1 - \exp [\ -4.18 \ (\ 10^{-3} \ )$$

$$\cdot \ (\ 53.53 \ x \ 1066 \ ) \ 0.42 \ ]$$

$$= 0.373$$

$$Sh_c = (\ 309.73 - 75.01 \ ) \ x \ 0.373 + 75.01$$

$$= 162.62$$

$$\frac{k_o d_p}{D_c} = 162.62$$

$$k_o = \frac{9.38 \times 10^{-10} \ x \ 162.62}{1.52 \times 10^{-3}}$$

$$= 10.04 \times 10^{-5} \ m/s$$

3.3 Partition Coefficient

For a given binary system, the partition coefficient is a function of the surfactant used. In the case of phenol extraction in water-kerosine system with span-80 as the surfactant. The relation, based on the experimental data from Teramoto et al., (1983), can be described as

$$X = 0.793 + 4.14X \qquad\qquad (3.3-1)$$

Where x is the volume fraction of span 80 to emulsion (membrane + internal phase).

The application range is that $0 < x < 0.05$

3.4 Diameter of Emulsion Drops

The drop sizes are not uniform, rather they have some kind of distribution lying between normal and Maxwell distribution (Teramoto 1983). In the same paper, it was demonstrated that Sauter's diameter could adequately describe the system.

The Sauter's diameter is difined as

$$d = \frac{\sum_i n_i d_{pi}^3}{\sum_i n_i d_{pi}^2} \qquad\qquad (3.4-1)$$

IV. Results and Discussion

The experimental data by Teramoto et al. (1983) are used to compare with the models developed in Chapter II. Globule diameters and partition coefficients were measured before experimental run. Diffusivities and mass transfer coefficients were estimated by the correlations in Chapter III.

The value of q is estimated as 1280 by Wang (1983). Having all the parameter values, we can calculate the external phase phenol concentration by the models developed in Chapter II.

4.1 Models Comparison

The parameter q in Model I means the ratio of the extractant in the internal phase to the membrane phase. The higher value of q means a faster extraction process. But it is obvious that q would be affected by the reactive reagent in the internal phase, thus can not be a constant.Fig. 4.1-1 to Fig.4.1-4 confirmed this conclusion. During the early stage of the separation, q has a smaller value than that in the later stage. The numerical value of q range from 50 to 500. The equilibrium constant for phenol reacting with sodium hydroxide is 1.1×10^4 (Morrison et al., 1966). q equals to 3,300 which too high to be realistic. However, it is very easy to see on Table 4.1-1 that Model II makes a great improvement on the predicting the separa-

Table 4.1-1   Error comparison between models and experimental
data (parameters values are listed on Table
4.1-2 and Table 4.1-3)

Time	h_{exp}	$h_{model\ I}$	$h_{model\ II}$	Error$_{model\ I}$	Error$_{model\ II}$
(1). C = 0.0212 N					
0.25	0.622	0.625	0.360	0.45	72.8
0.50	0.493	0.494	0.161	0.20	206.2
1.00	0.381	0.360	0.079	5.50	382.2
2.00	0.270	0.242	0.047	10.40	474.5
5.00	0.167	0.132	0.029	20.96	478.9
10.00	0.152	0.083	0.022	45.40	590.9
(2). C = 0.0160 N					
0.25	0.563	0.551	0.358	3.20	57.3
0.50	0.448	0.434	0.172	3.13	160.5
1.00	0.322	0.289	0.078	10.20	312.8
2.00	0.181	0.173	0.047	4.40	285.1
5.00	0.070	0.082	0.029	17.10	141.4
10.00	0.052	0.047	0.021	9.62	147.6

tion behavior. It also reflects the effect of the chemical

reagent. It, in fact, can predict the response of the exter

nal phase concentration to the changes of almost every

physical and/or chemical properties. But, as showed on Fig.

4.1-5 to Fig. 4.1-8, when external phase concentration dec

reases, the accuracy of the model decreases. This disadvan

tage also showed on Fig. 4.3-2 to Fig. 4.3-4. Based on these

evidences, it is suggested that Model II can not be applied

with confidence when extractant in source phase has a conce-

ntration lower than 0.01N. The operating conditions, except

for external phase concentration, and the parameters used

for the experiment are listed in Table 4.1-2 and Table 4.1-

3.

Table 4.1-2

Experimental Conditions for Phenol Removal

Vol. of membrane phase, ml	50
Vol. of internal phase, ml	50
Vol. of external phase, ml	650
Con. of NaOH in internal phase, N	0.3
Globule diameter, cm	0.152

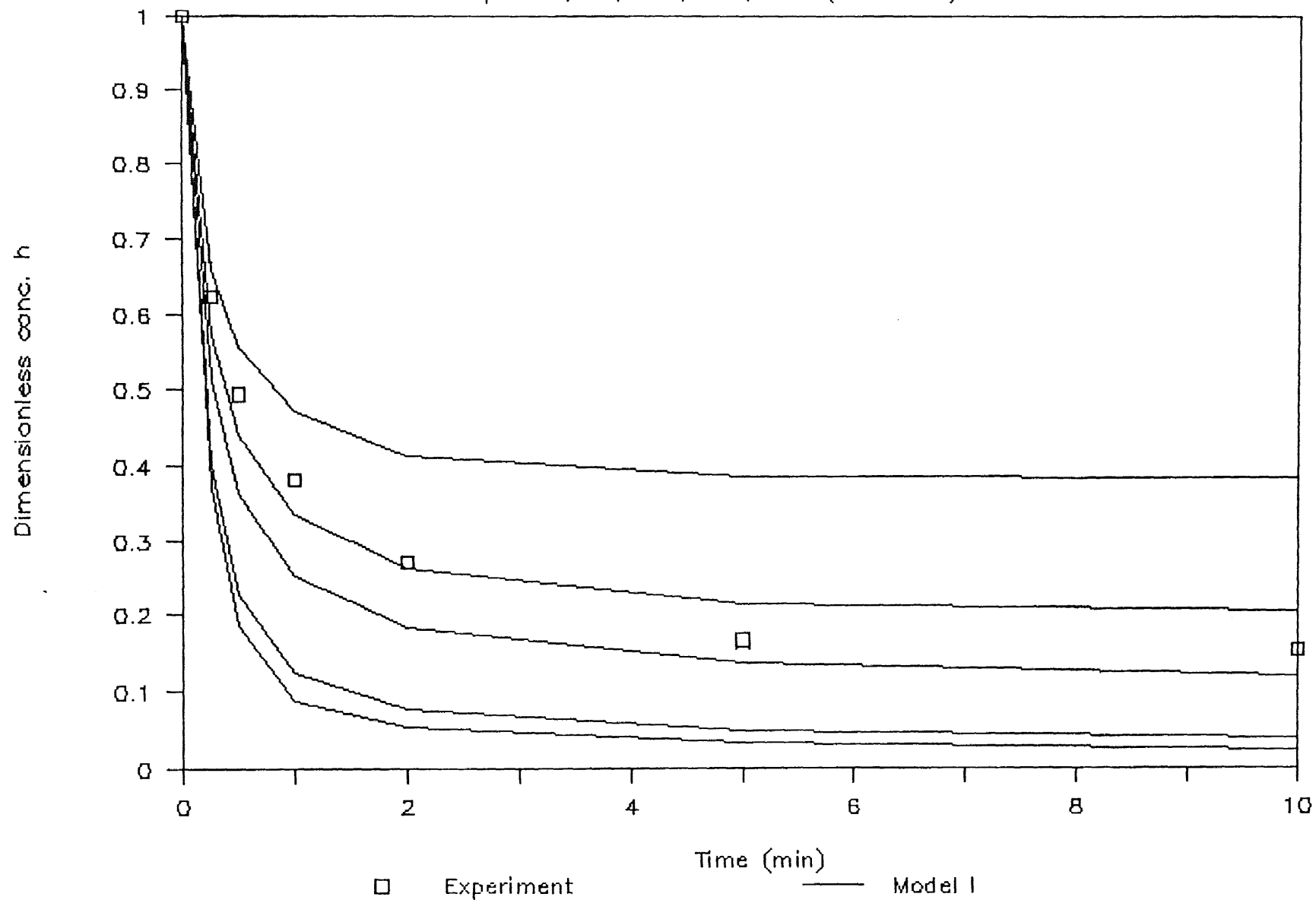Fig. 4.1-1   h vs. time at Ceo=0.0212N
q = 20, 50, 100, 500, 1000(downward)

Dimensionless conc. h

Time (min)

□   Experiment   ———— Model I

34

Fig. 4.1-2 h vs. time at Ceo=0.0160N

q = 20, 50, 100, 500, 1000(downward)

Dimensionless conc. h

Time (min)

□　　Experiment　　　　　　———　　Model I
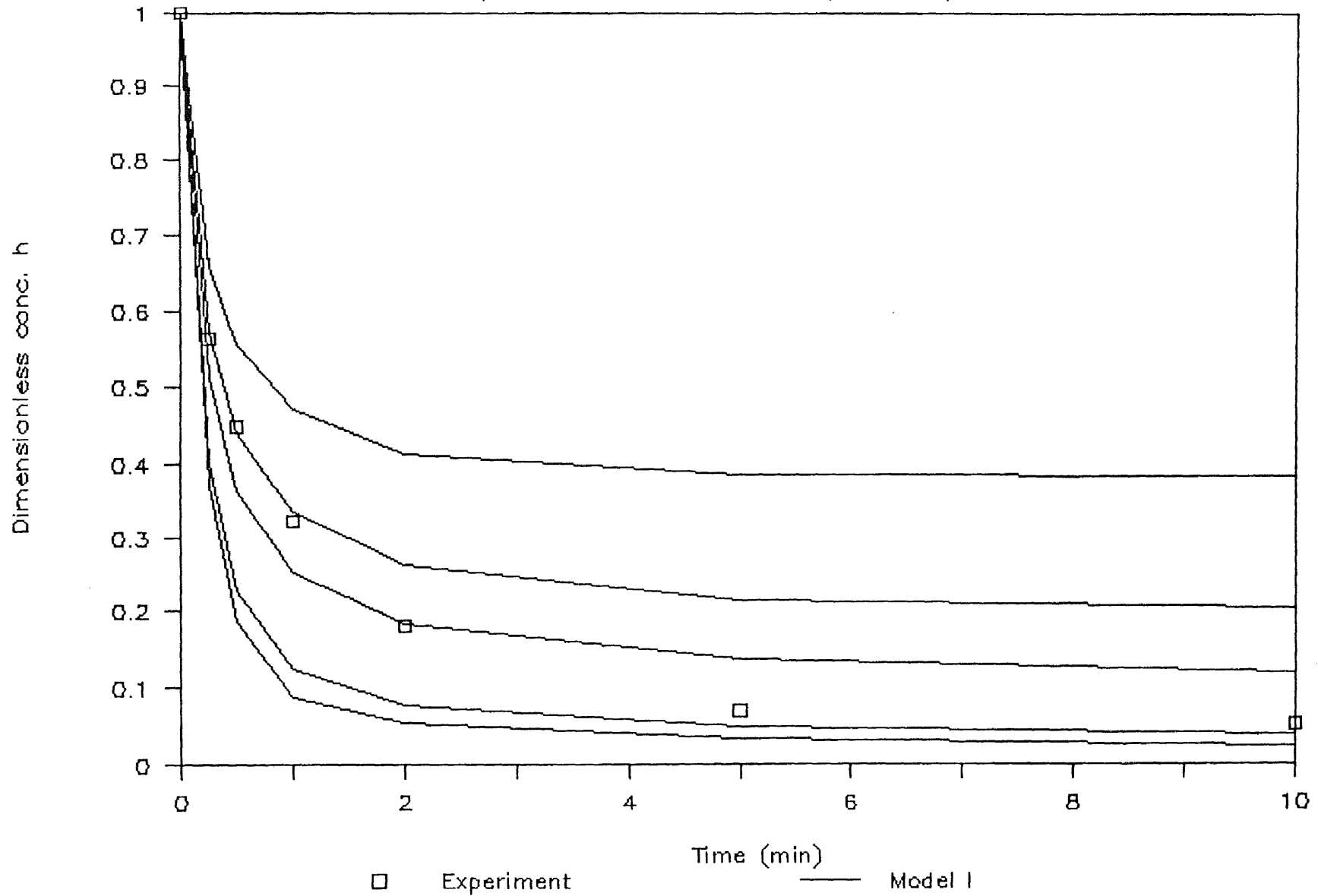
Fig. 4.1-3 h vs. time at Ceo=0.0106N

q = 20, 50, 100, 500, 1000(downward)

Dimensionless conc. h

Time (min)

□   Experiment   ———   Model I

36
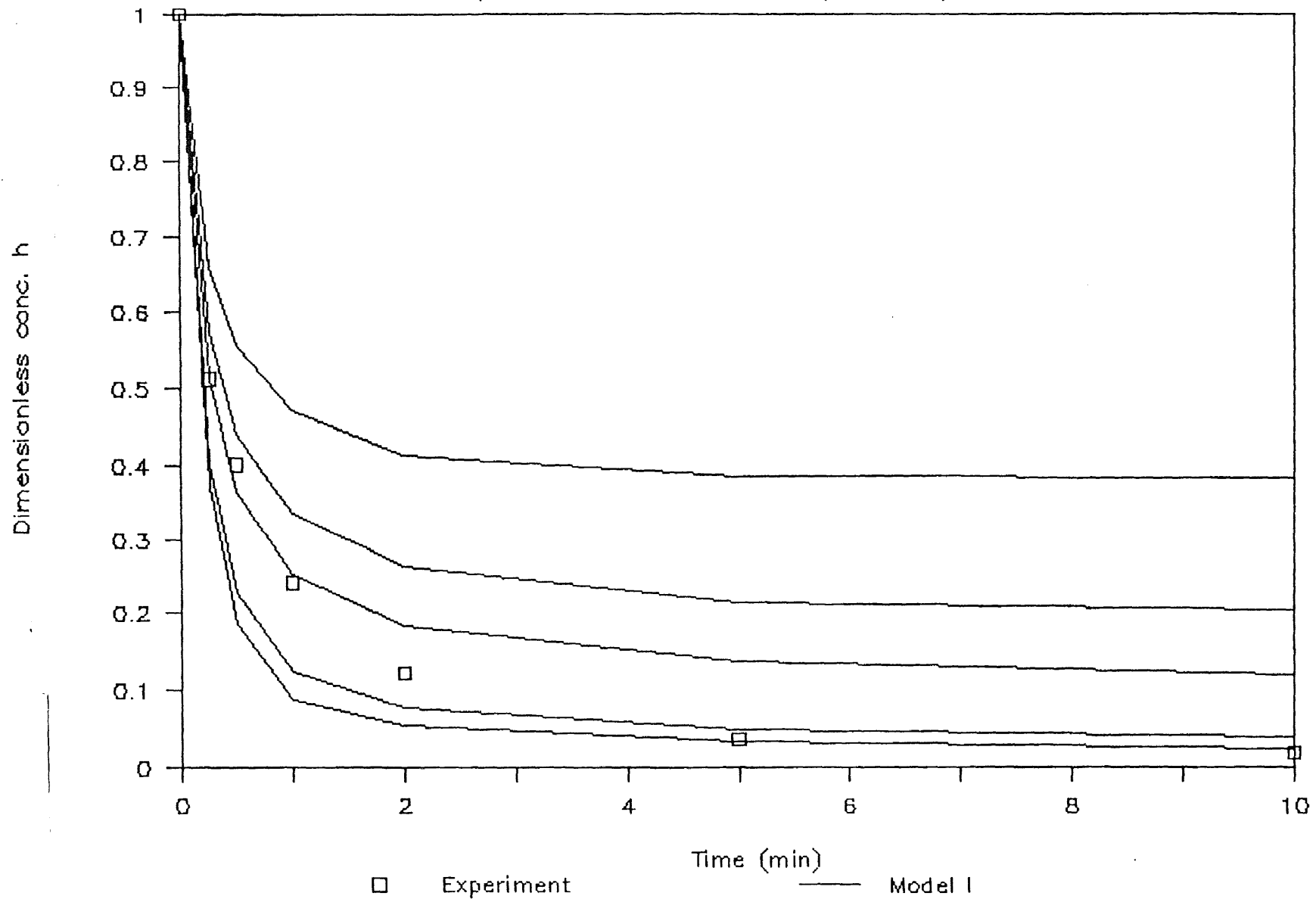
Fig. 4.1-4   h vs. time at Ceo=0.0053N

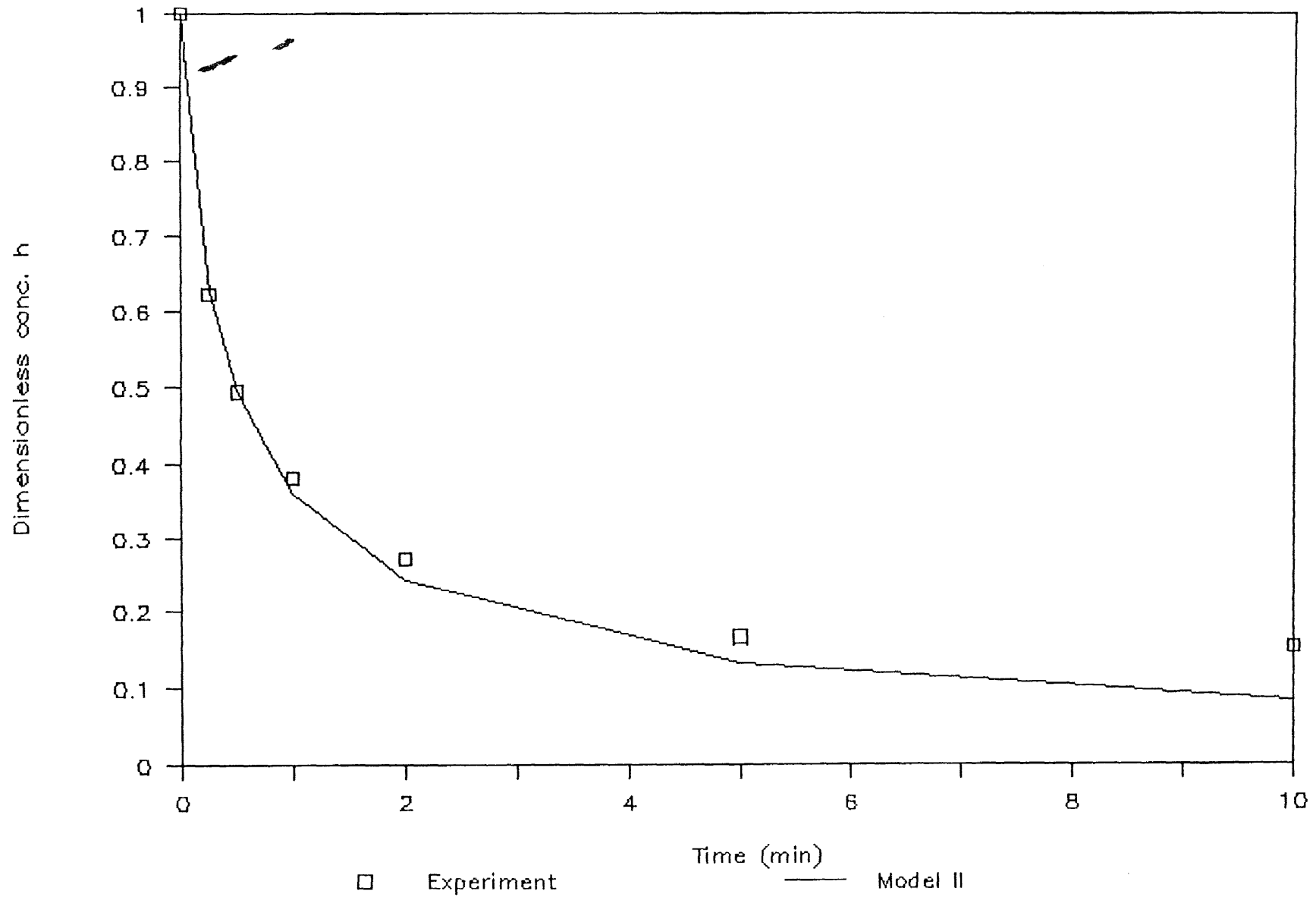q = 20, 50, 100, 500, 1000(downward)

□   Experiment   ——— Model I
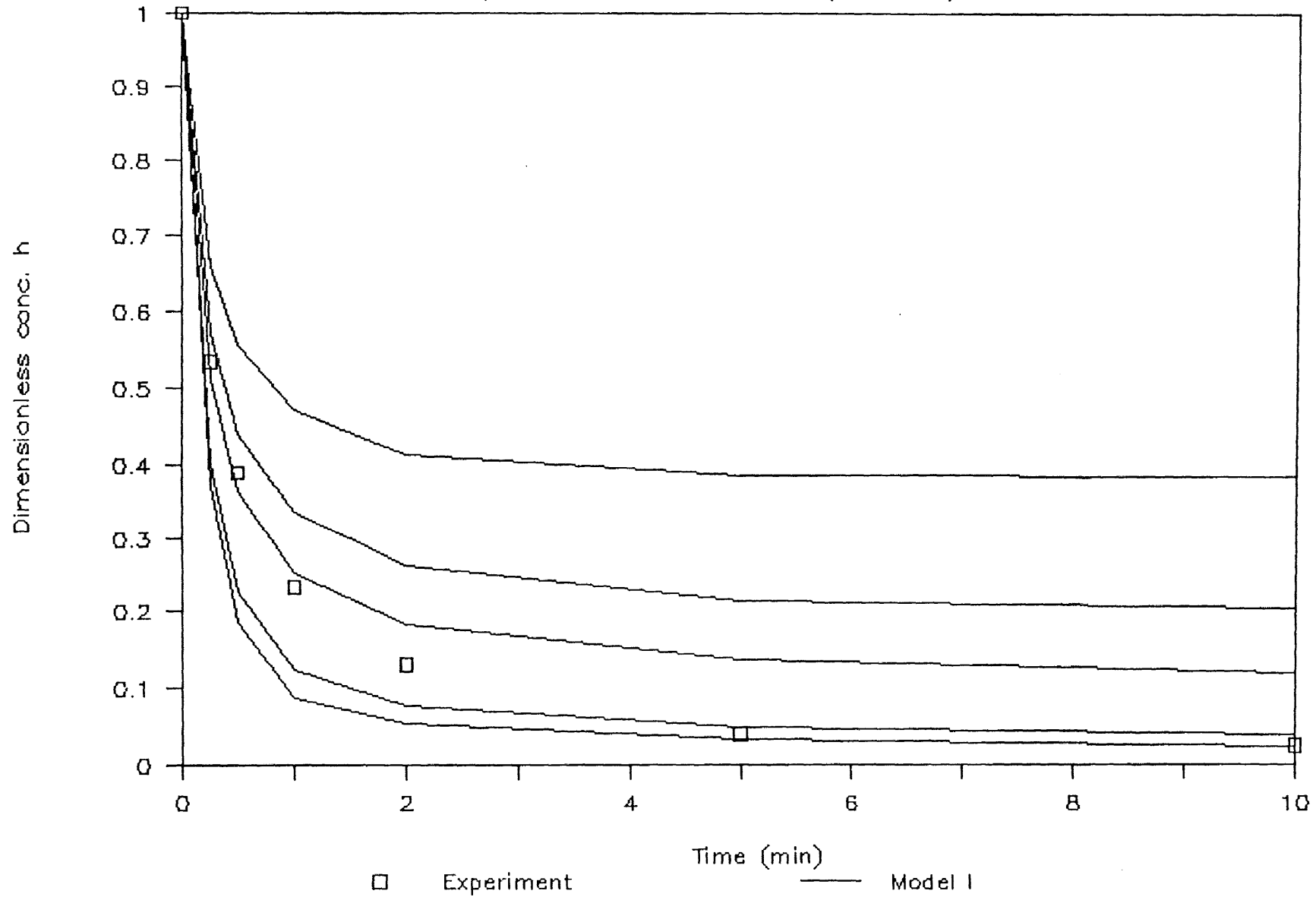
Fig. 4.1-5 h vs. time at Ceo=0.0212N

Fig. 4.1-6   h vs. time at Ceo=0.0160N
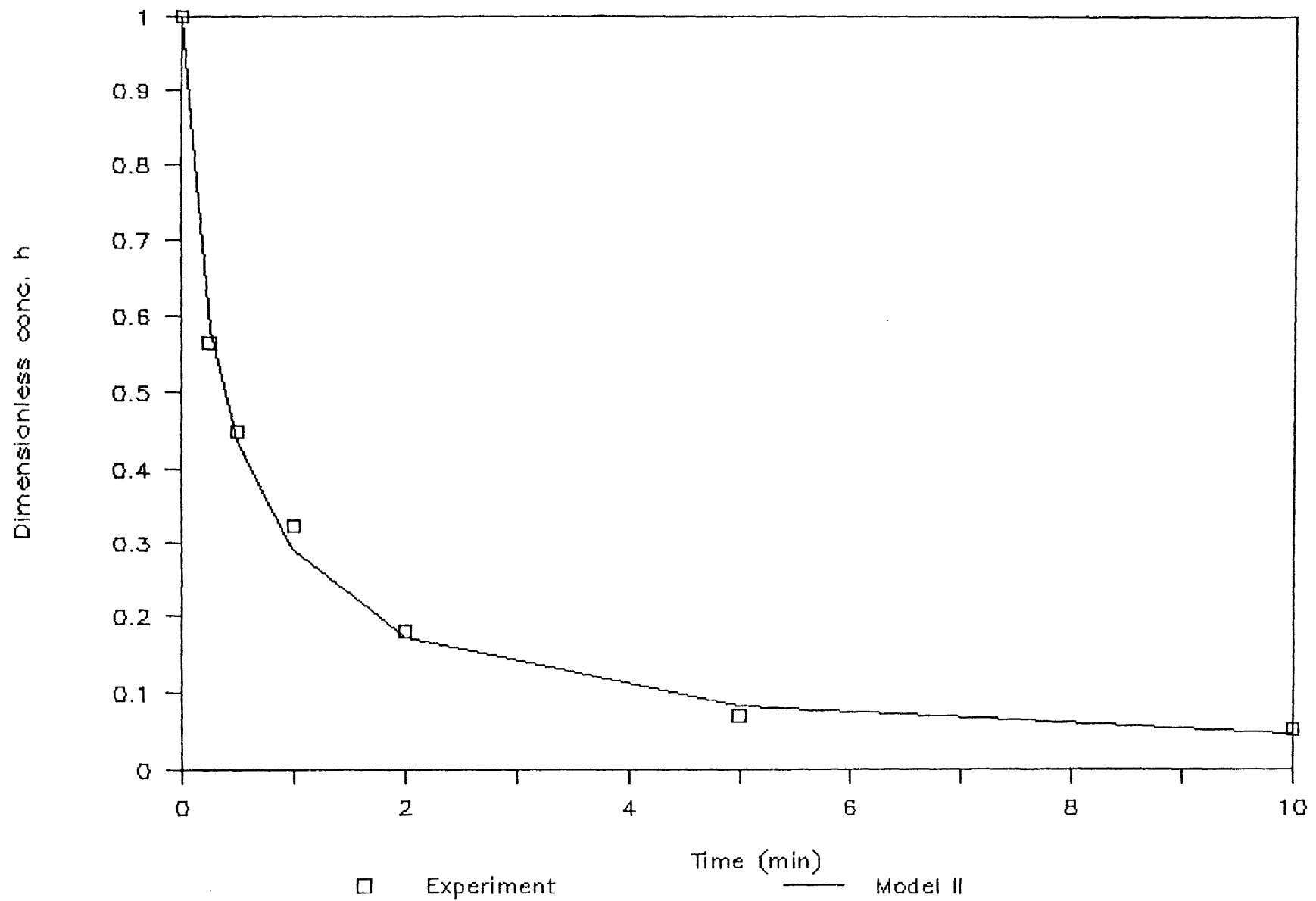
Fig. 4.1-7 h vs. time at Ceo=0.0106N

□   Experiment   ——— Model II

40
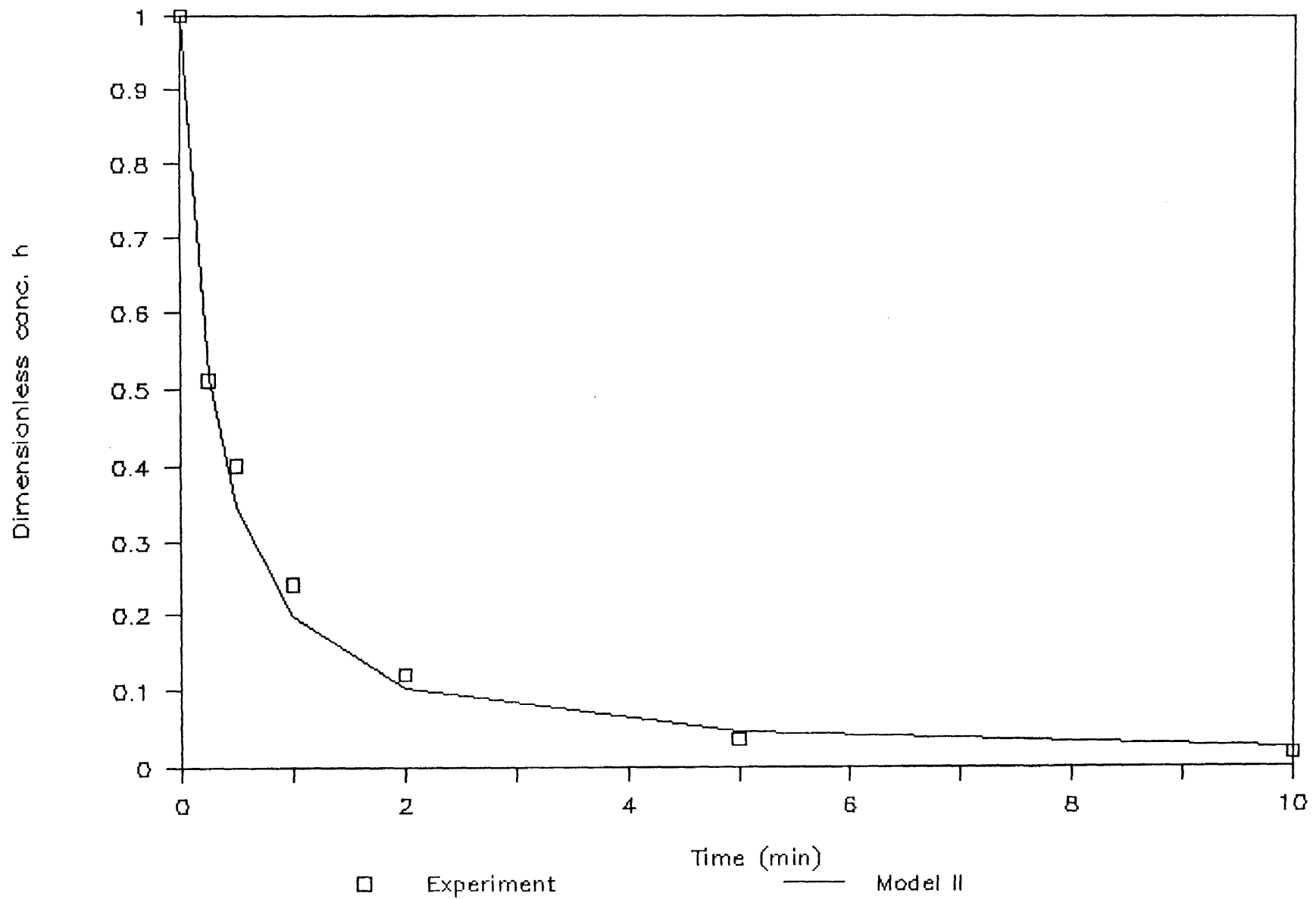
Fig. 4.1-8 h vs. time at Ceo=0.0053N

Dimensionless conc. h

Time (min)

□ Experiment ———— Model II

41
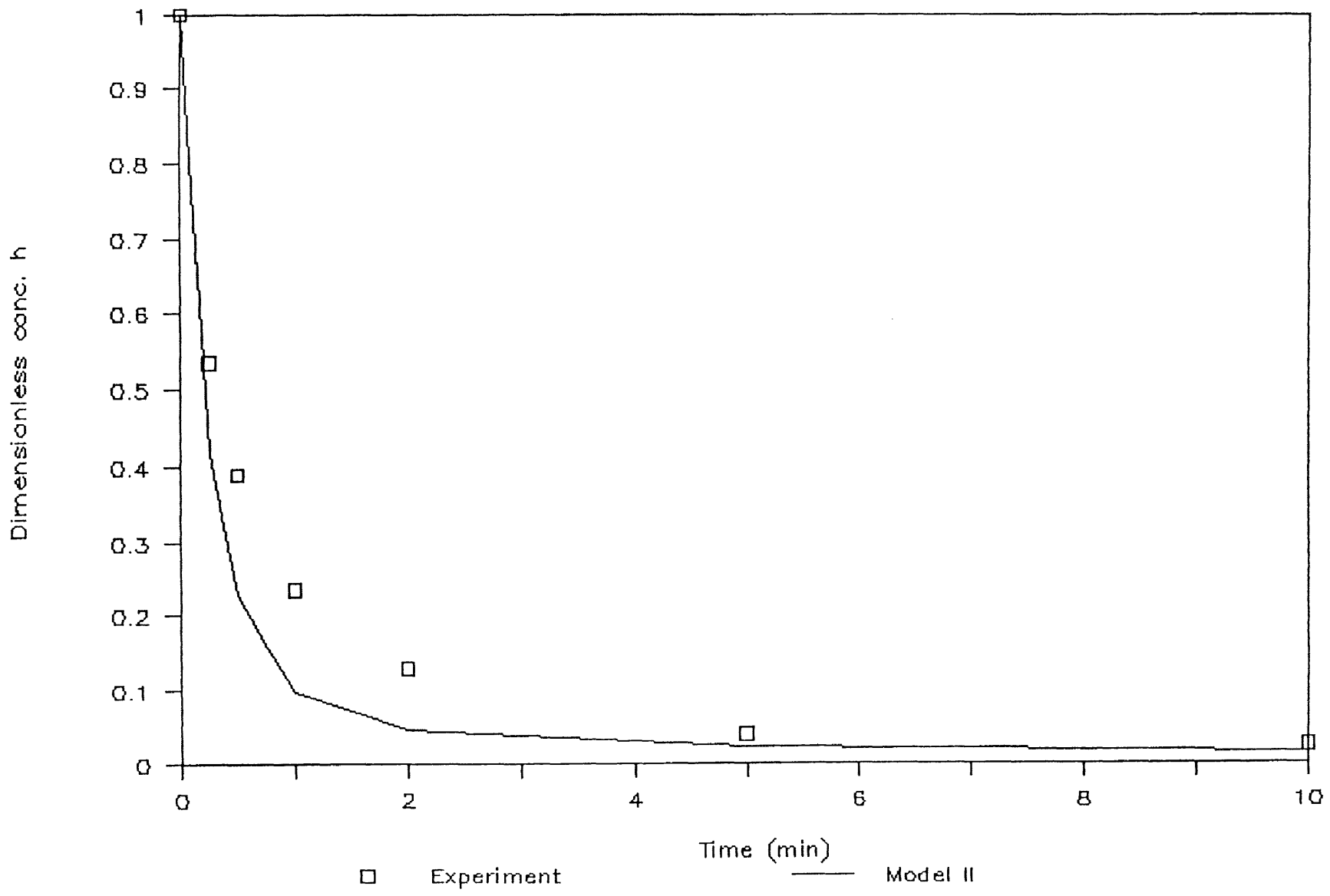
Table 4.1-3

Parameter Values for Phenol Removal

e	0.5
f	0.1333
k , cm/s x10^2	0.758
R, cm	0.076
a (a = a_i = a_o)	1

The diffusivity slightly changes with the extractant, in external phase, concentration. Table 4.1-4 lists data used in this section.

Table 4.1-4

Extractant concentration, N	0.0212	0.0160	0.0106	0.0053
D_{eff} , cm^2/s x 10^5	2.10	2.22	2.46	3.12

4.2 Effect of the Globule Radius

For the same amount of emulsified globule, smaller radius means larger mass transfer area, which is a positive factor as for the separation. But there is also a negative effect – the smaller radius will result in smaller mass transfer coefficient (Chapter 3.2).

emulsified globules as the computation base. When R changes from 0.076 cm to 0.052 cm (two operating conditions), the mass transfer area increase 46%, but the external mass transfer coefficient reduces 18%. The net effect, mass transfer area times mass transfer coefficient, would have about 20% increment.

The experimental result is 36% increment after 1 min operaion.

The experimental conditions for three cases and their parameters are summarized in Table 4.2-1 and 4.2-2. Fig. (4.2-1) shows the experimental data of the three cases. Figs. (4.2-1) and (4.2-4) demonstrate the predictions of the Model II developed previouly along with the experimental data.

Table 4.2-1

Experimental Conditions for Phenol Removal

experiment number	1	2	3
Vol. of membrane phase, ml	50	50	50
Vol. of internal phase, ml	50	50	50
Vol. of external phase, ml	650	650	650
Con. of NaOH in internal phase, M	0.3	0.3	0.3
Con. of PhOH in external phase, N	0.0106	0.0106	0.0106
Globule diameter, cm	0.152	0.102	0.082

Fig. 4.2-1   h vs. time at different R

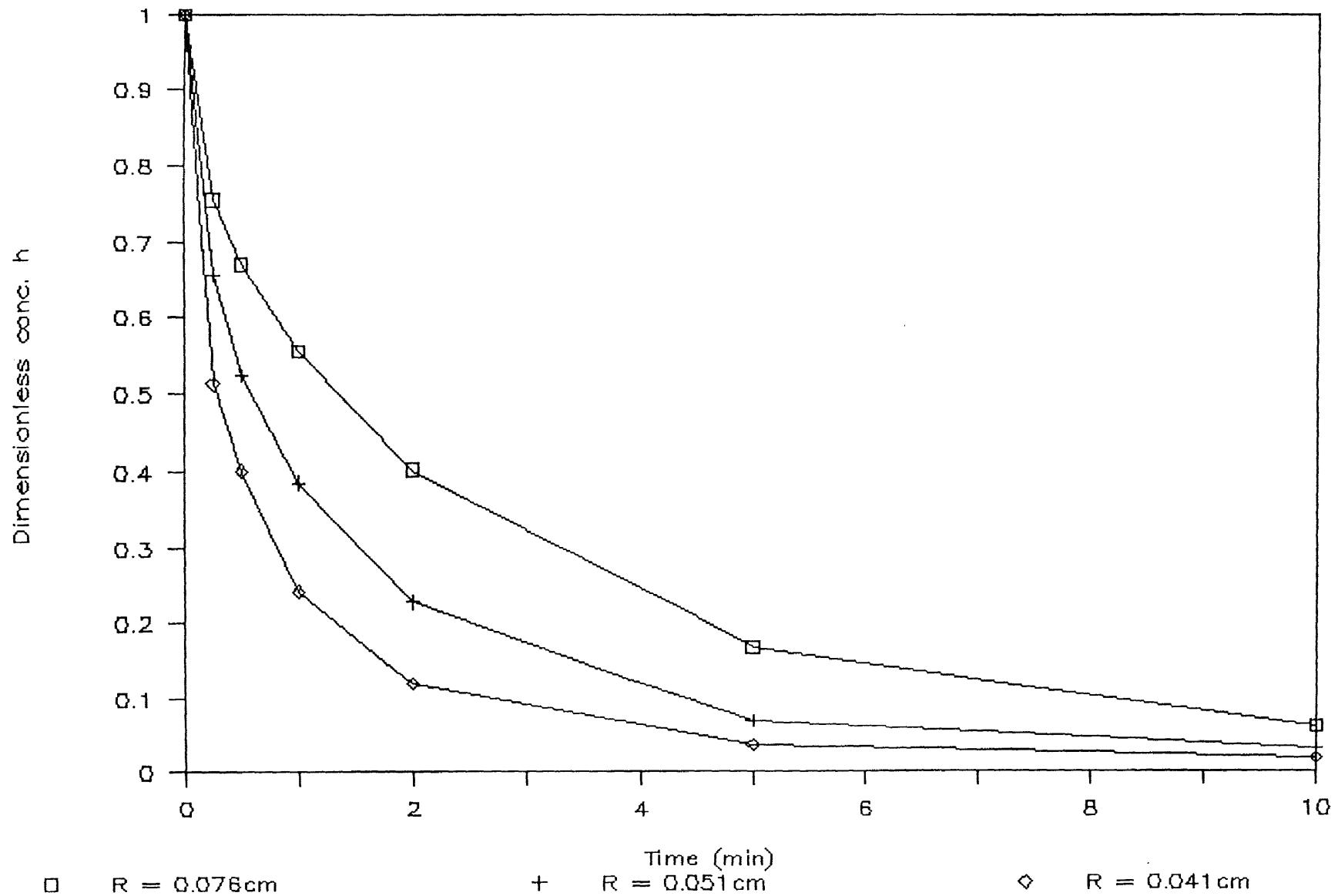□   R = 0.076 cm   +   R = 0.051 cm   ◇   R = 0.041 cm

Fig. 4.2-2 h vs. time at R = 0.076cm
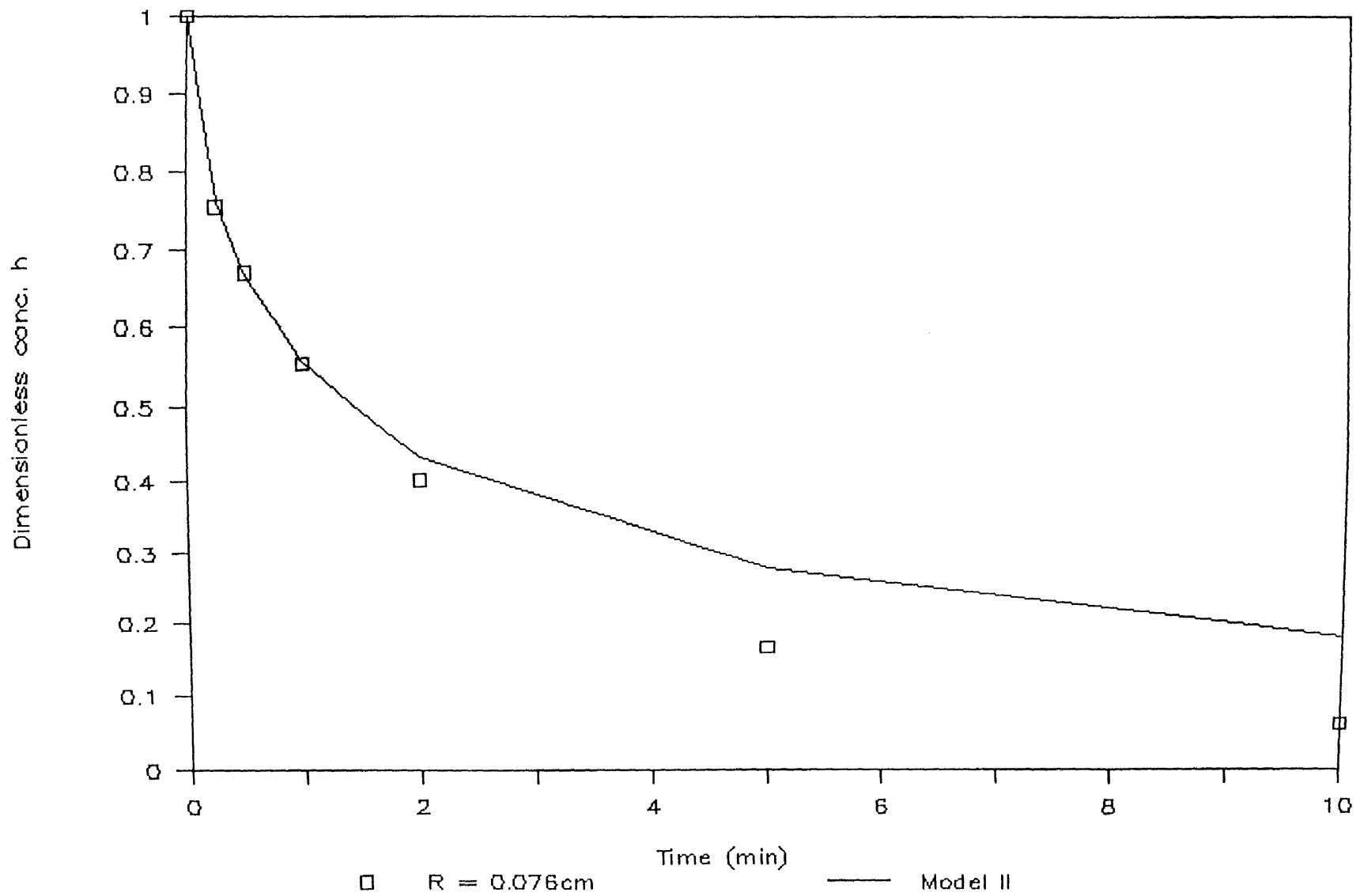
Fig. 4.2-3   h vs. time at R = 0.051cm

46
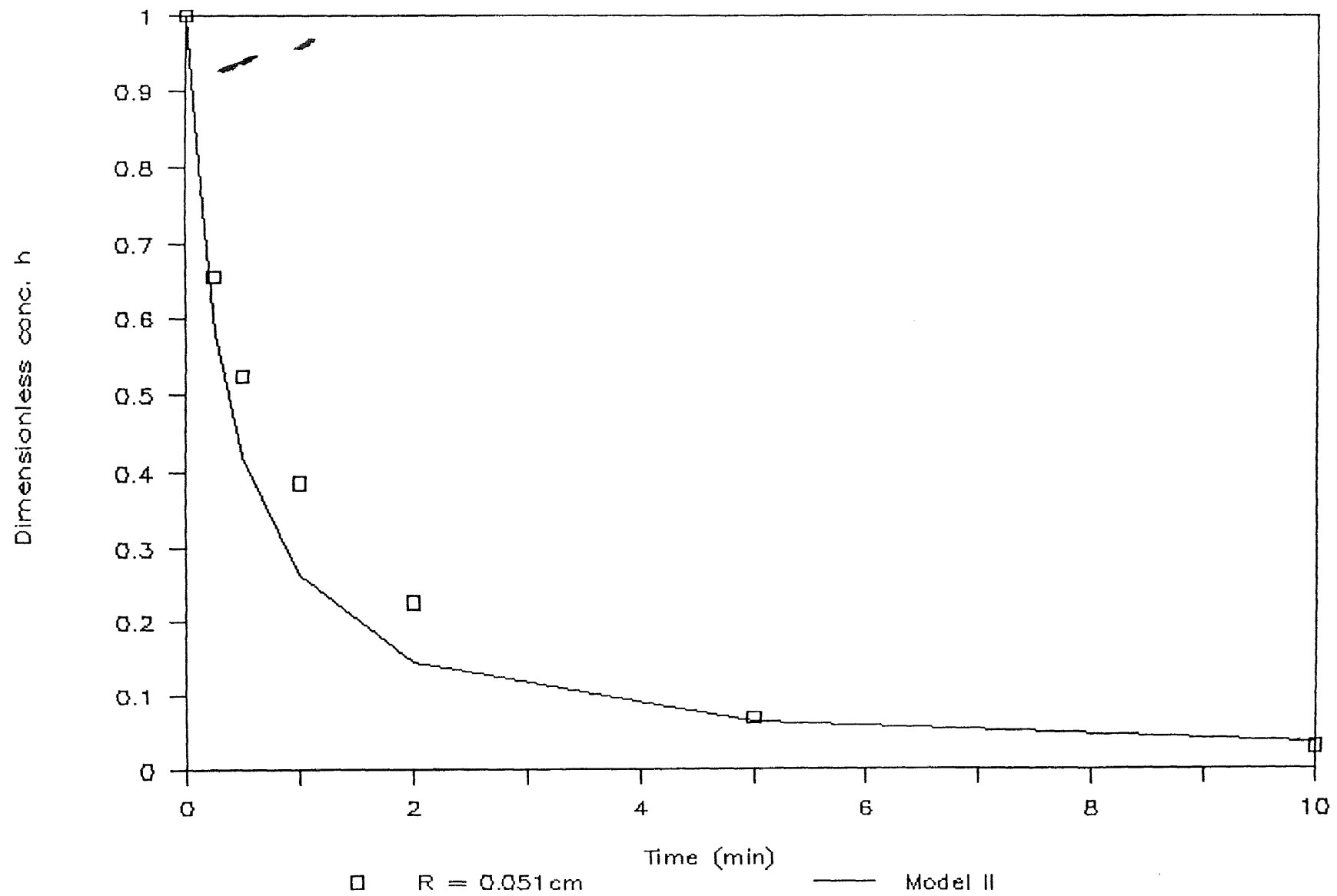
Fig. 4.2-4   h vs. time at R = 0.041 cm

□   R = 0.041 cm   —— Model II

47
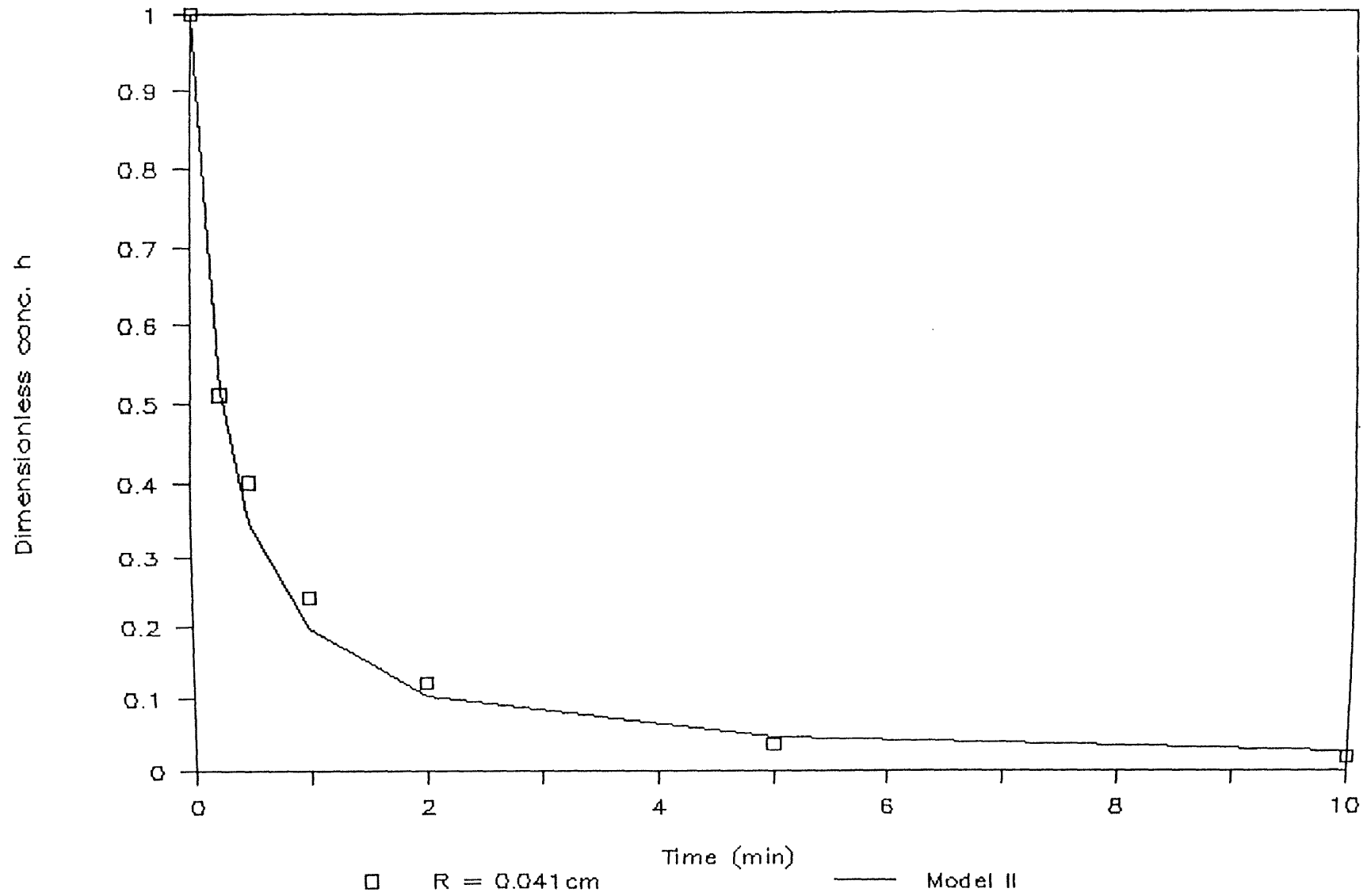
Table 4.2-2

Parameter Values for Phenol Removal

experiment number	1	2	3
e	0.5	0.5	0.5
f	0.1333	0.1333	0.1333
D_{eff} , cm /s x 10^5	2.46	2.46	2.46
K , cm/s x 10^2	1.034	0.846	0.758
R, cm	0.076	0.052	0.041
a (=a_i = a_o)	1.0	1.0	1.0

4.3 Effect of the Initial Concentration of NaOH

Chemically, higher NaOH concentration means higher reaction rate. Obviously, this is a positive factor. Also, if we look into the parameters, as showed in Chapter III, higher NaOH concentration gives higher D_{eff} and smaller radius, both of them can increase the phenol extraction rate.

Experimental conditions and parameters are summarized on Table 4.3-1 and 4.3-2. Fig. (4.3-1) shows three sets of experimental data. Fig. (4.3-2), (4.3-3) and (4.3-4) shows the comparison between theoretical and experimental results.

Table 4.3-1

Experimental Conditions for Phenol Removal

experiment number	1	2	3
Vol. of membrane phase, ml	50	50	50
Vol. of internal phase, ml	50	50	50
Vol. of external phase, ml	650	650	650
Con. of NaOH in internal phase, M	0.1	0.2	0.3
Con. of PhOH in external phase, N	0.0016	0.0016	0.0016
Globule diameter, cm	0.104	0.100	0.082

Table 4.3-2

Parameter Values for Phenol Removal

experiment number	1	2	3
e	0.5	0.5	0.5
f	0.1333	0.1333	0.1333
D_{eff} , cm^2/s x 10^5	3.45	4.52	4.95
k , cm/s x 10^2	0.884	0.840	0.758
R, cm	0.052	0.050	0.041
a	1.0	1.0	1.0

Fig. 4.3-1. h vs. time at different Cio

Dimensionless conc. h

Time (min)

□   Cio = 0.1 M   +   Cio = 0.2 M   ◇   Cio = 0.3 M

50

Fig. 4.3−2. h vs. time at Cio = 0.1 M

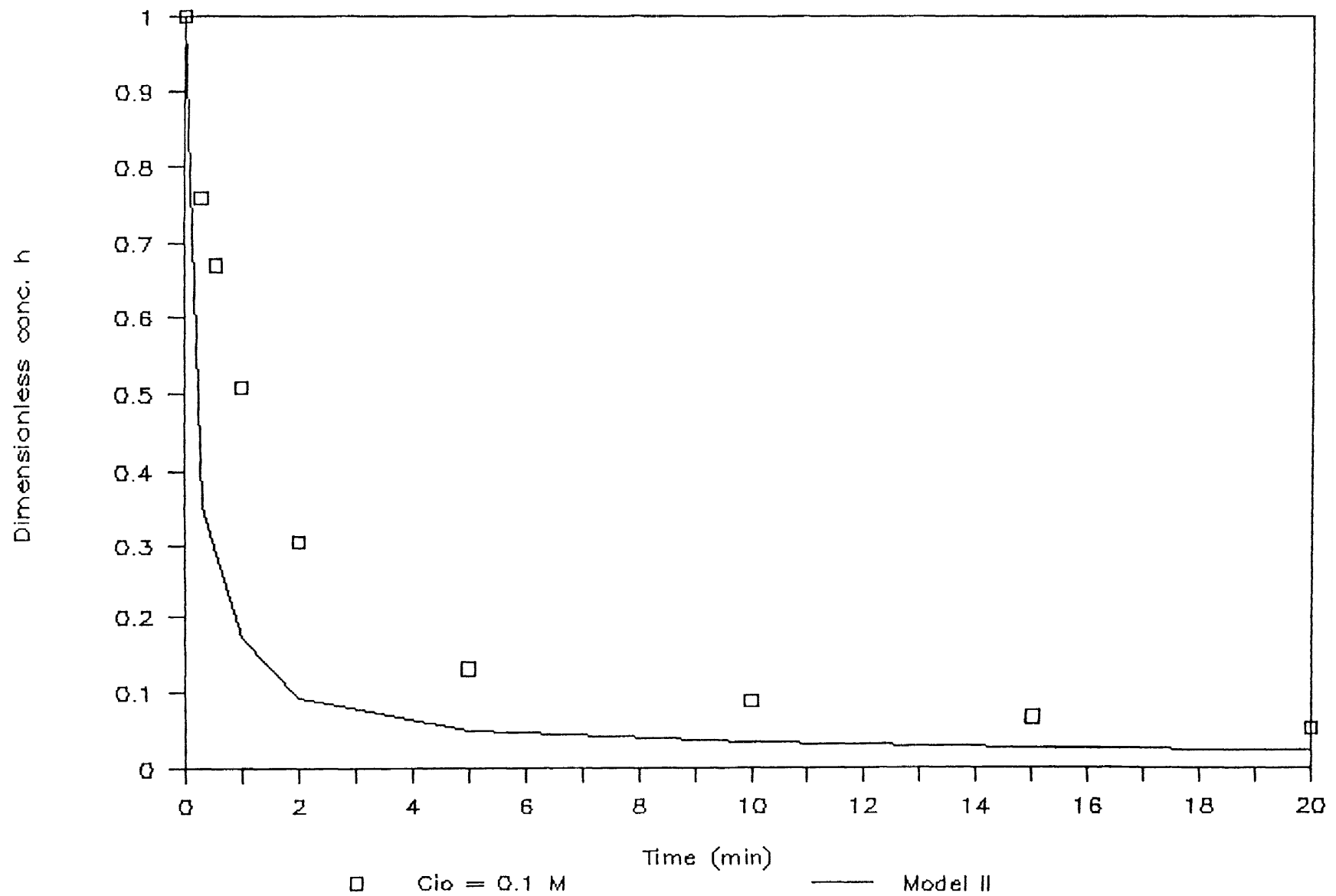Dimensionless conc. h

Time (min)

□   Cio = 0.1 M   ——— Model II

51
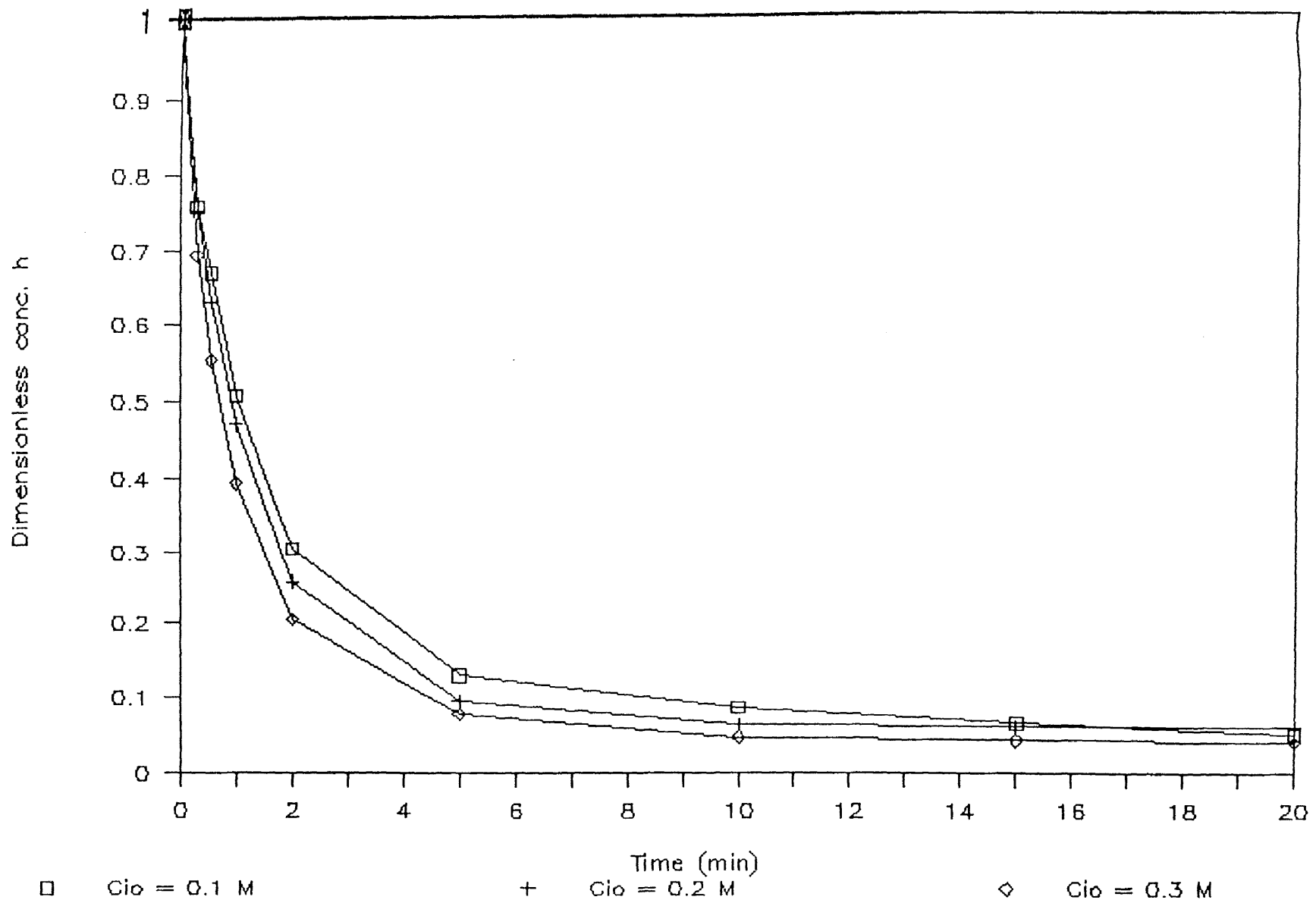
Fig. 4.3—3. h vs. time at Cio = 0.2 M

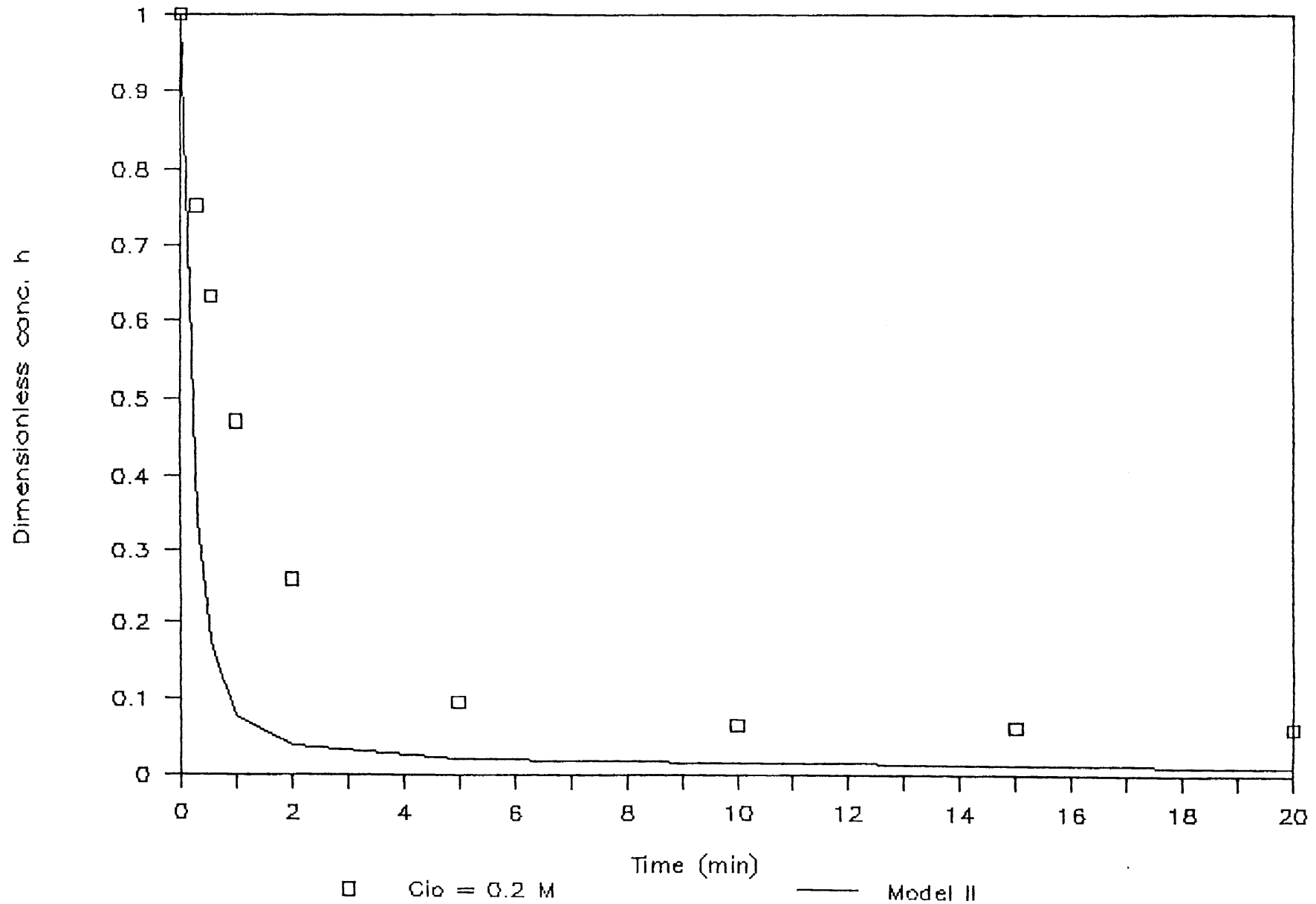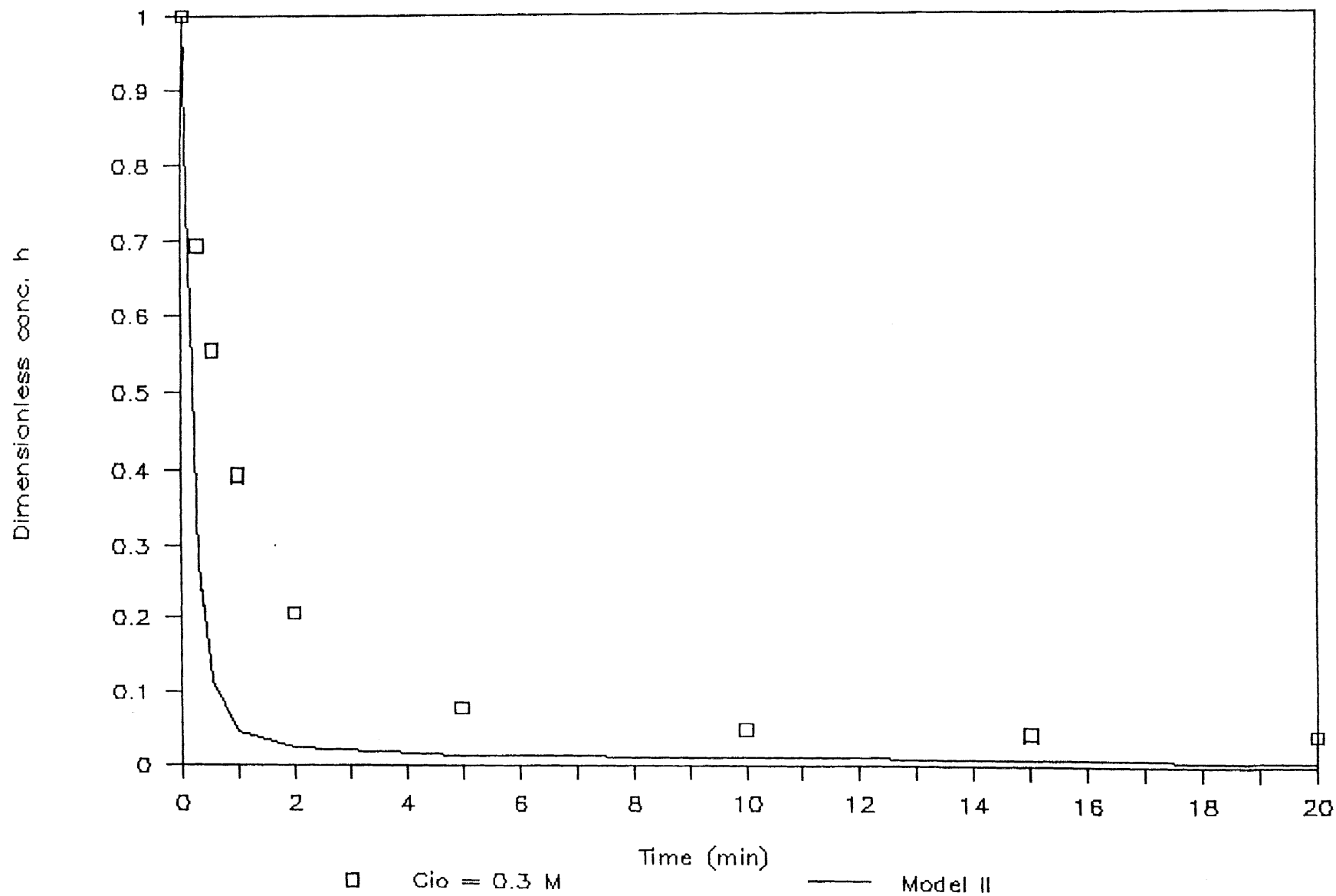Fig. 4.3-4. h vs. time at Cio = 0.3 M

4.4 Effect of the Initial Concentration of PhOH

This factor is not that obvious, because within the usual operating range, the globule radius is not affected by the concentration of PhOH. Based on Chapter III, D_{eff} increases only slightly as the PhOH concentration goes up. Table 4.4-2 and 4.4-2 summarized the experimental conditions and parameters. Fig. (4.3-2) to (4.3-5) show the comparison between theoretical and experimental results.

Table 4.4-1

Experimental Condition for Phenol Removal

experiment number	1	2	3	4
Vol. of membrane phase, ml	50	50	50	50
Vol. of internal phase, ml	50	50	50	50
Vol. of external phase, ml	650	650	650	650
Con. of NaOH in internal phase, M	0.3	0.3	0.3	0.3
Con. of PhOH in external phase, N	0.0212	0.0160	0.0106	0.0053
Globule dia., cm	0.152	0.152	0.152	0.152

Table 4.4-2

Parameter Value for Phenol Removal

experiment number	1	2	3	4
e	0.5	0.5	0.5	0.5
f	0.1333	0.1333	0.1333	0.1333
D_{eff} , cm^2/s x 10^5	2.10	2.22	2.46	3.12
k , cm/s x 10^2	1.034	1.034	1.034	1.034
R, cm	0.076	0.076	0.076	0.076
a	1.0	1.0	1.0	1.0

Fig. 4.4—1 h vs. time at different Ceo

Dimensionless conc. h

Time (min)

□   Ceo = 0.0212 N   ◇   Ceo=.0106N

+   Ceo=.0160N   △   Ceo = 0.0053 N

56
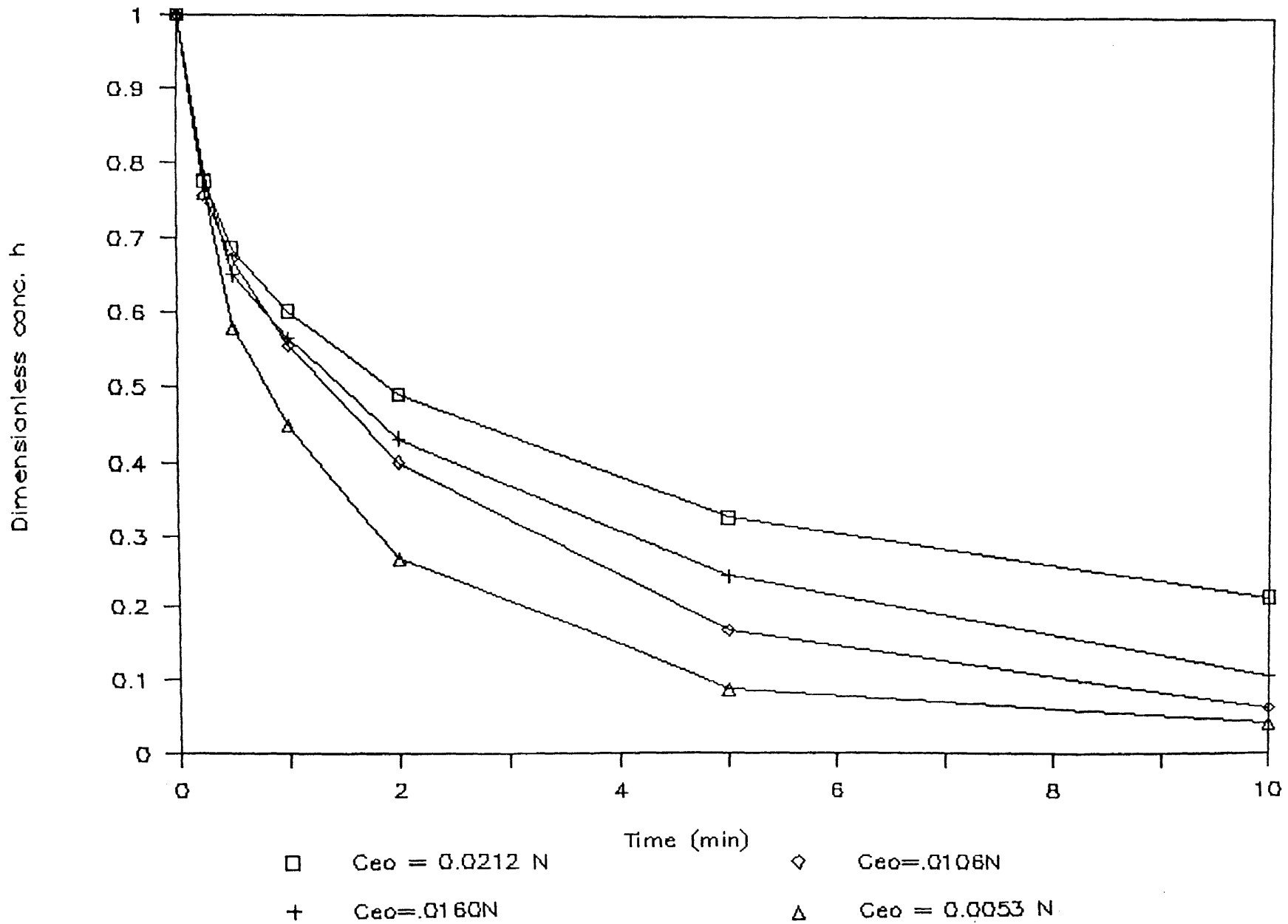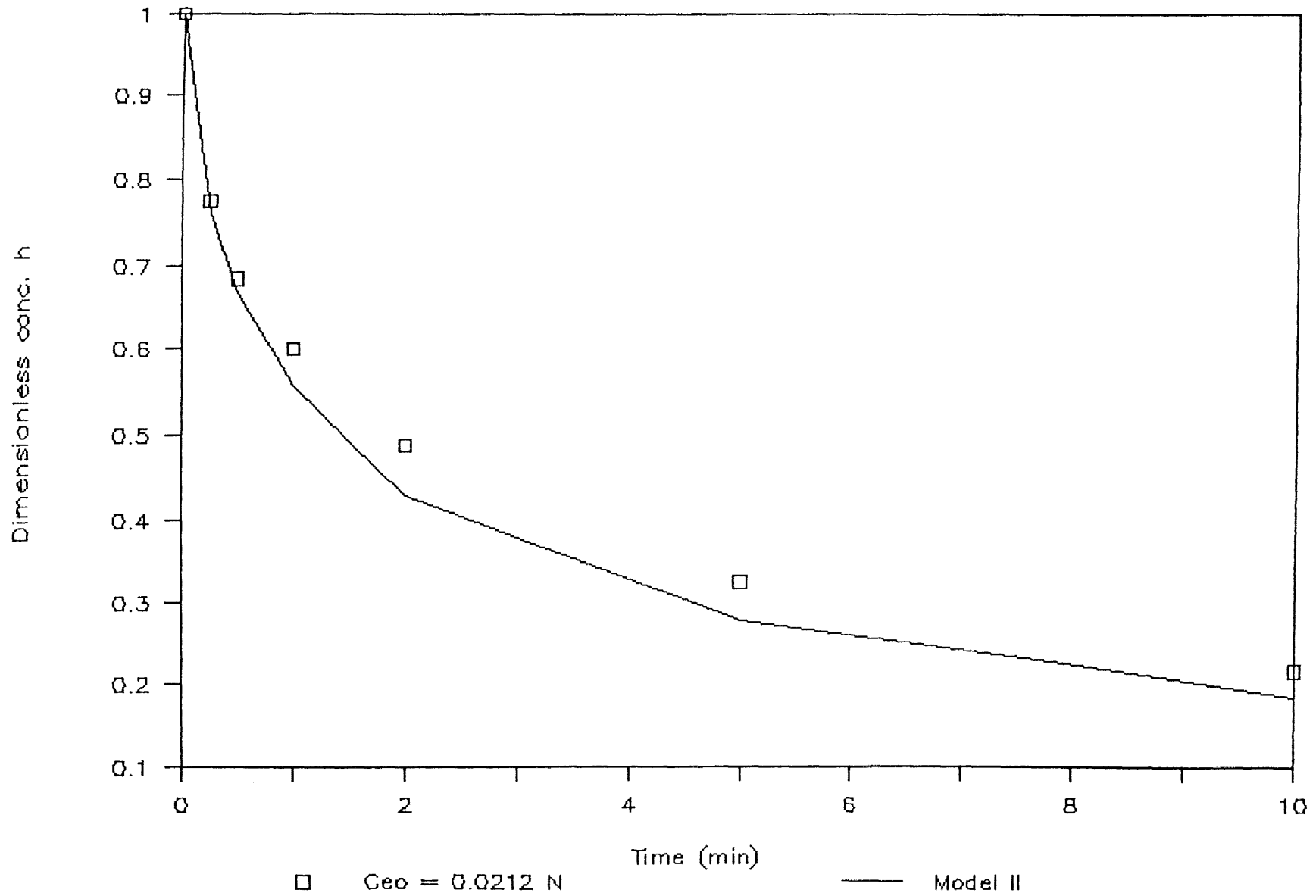
Fig. 4.4-2 h vs. time at Ceo=0.0212 N

Fig. 4.4-3   h vs. time at Ceo=0.0160 N

Dimensionless conc. h

Time (min)

□   Ceo = 0.0160 N   ——— Model II

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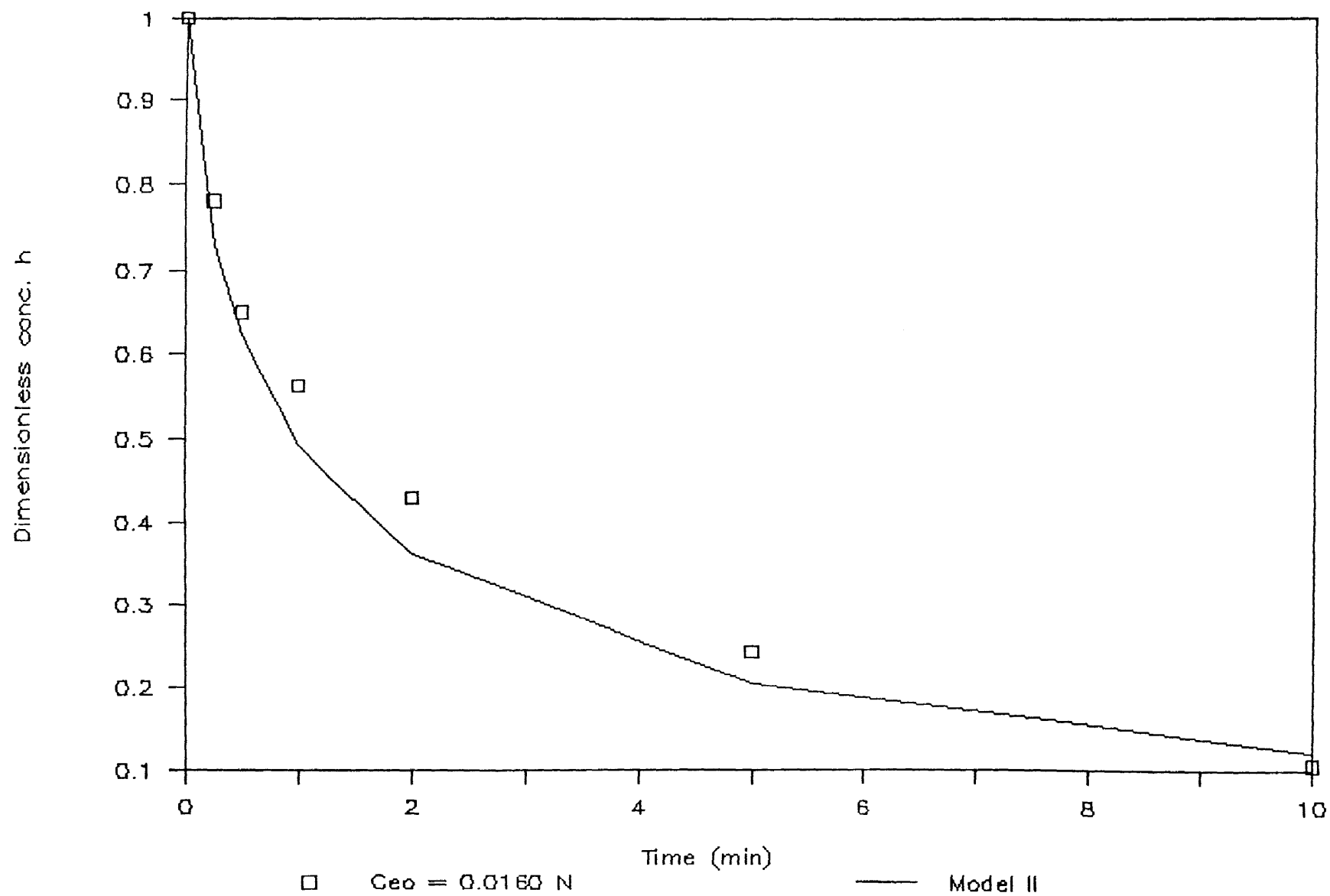
Fig. 4.4—4   h vs. time at Ceo=0.0106 N

Dimensionless conc. h

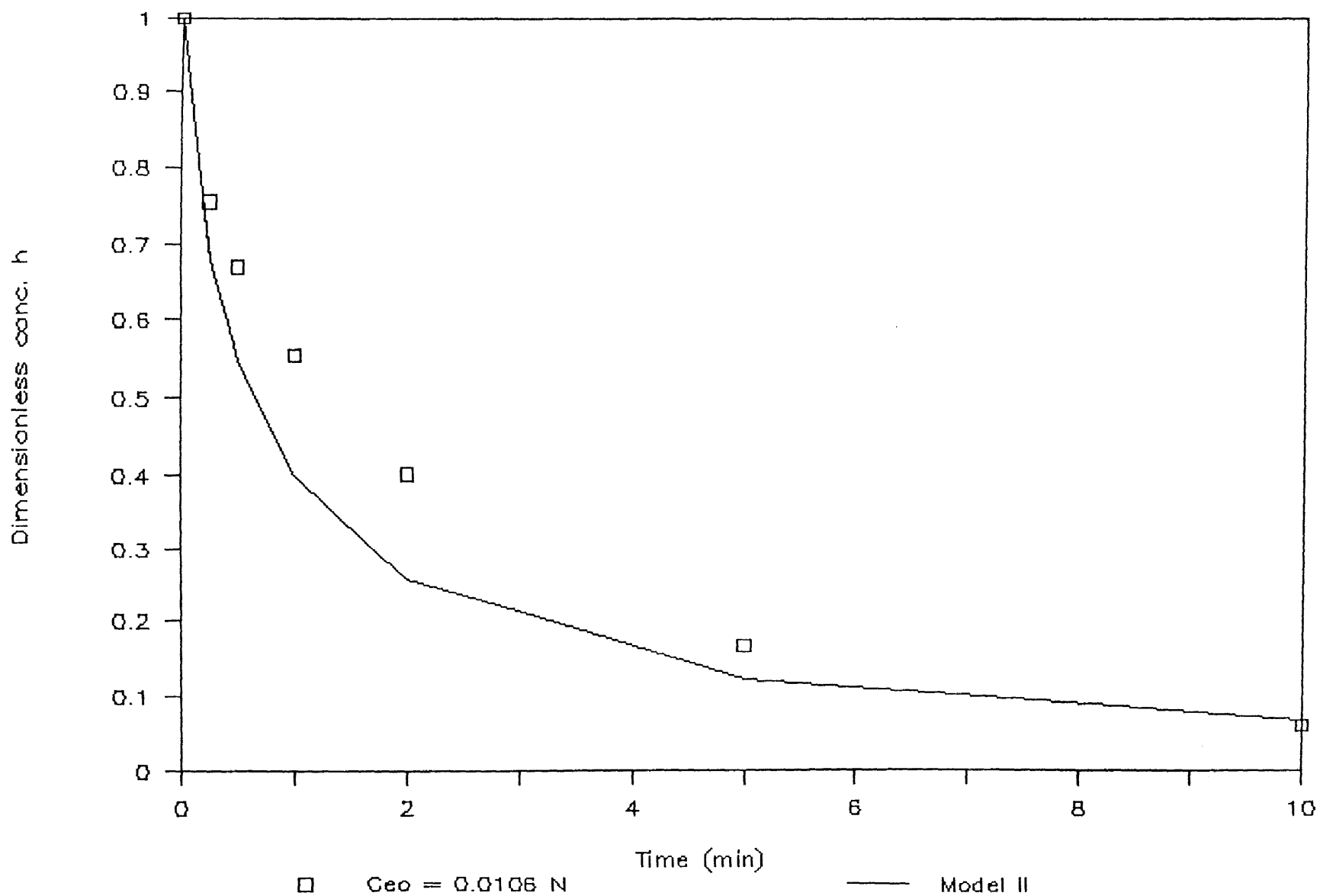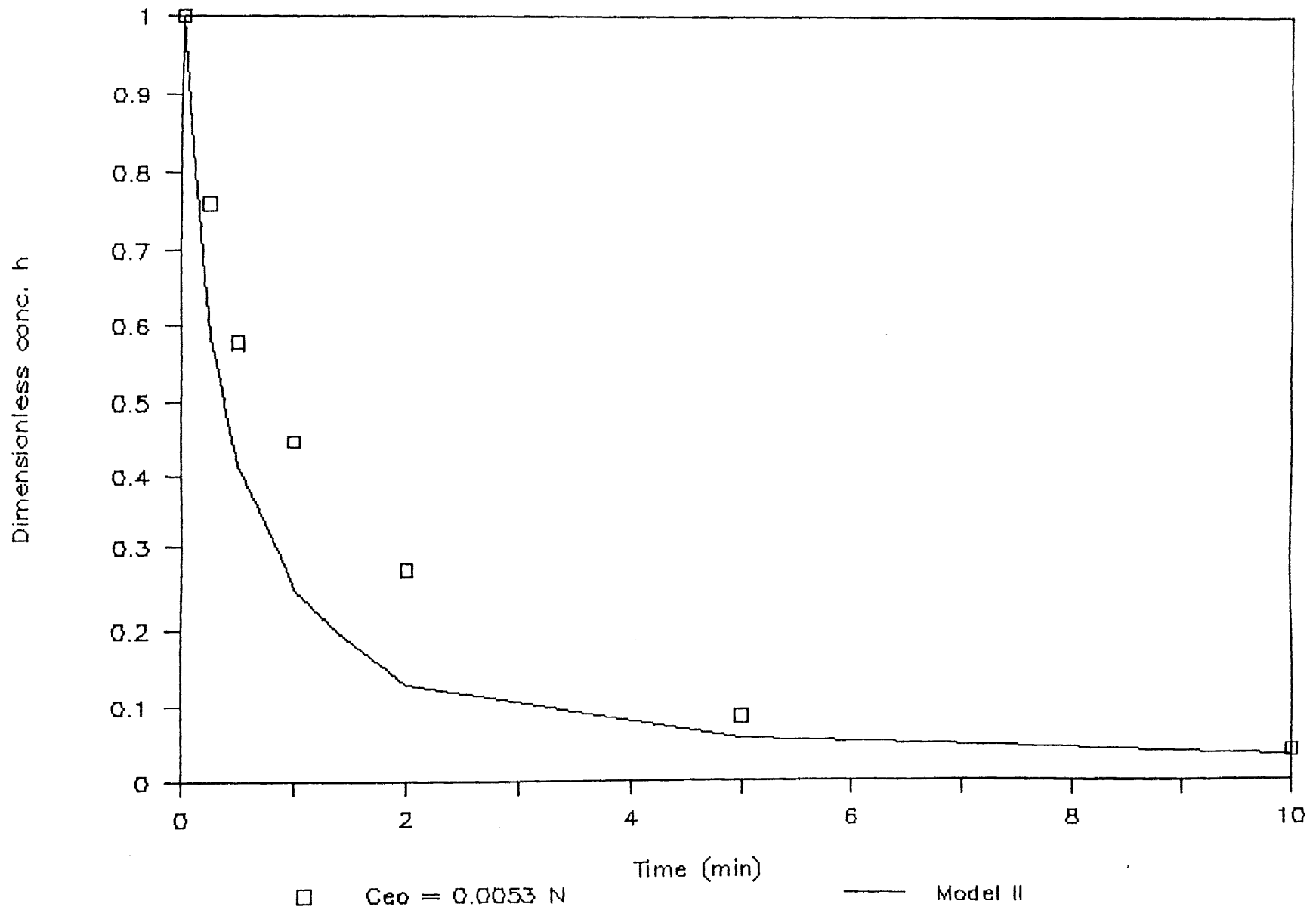Time (min)

□   Ceo = 0.0106 N   —— Model II

Fig. 4.4-5   h vs. time at Ceo=0.0053 N

60

V. Conclusion

There are several advantages of Model II comparing to the existing ones. Simplicity is a very important feature. It requires neither complicated mathematical computation nor a great amount of computer time, it can be applied to carrier mediated liquid membrane system just by changing the phase and chemical equilibrium constants, and above all, it can predict the extraction rate without the need of actual experimental run. No adjustable parameters in Model II are required. All parameters can be determined independently - either by simple experiments or by correlations. There are, unfortunately, two major disadvantages. First, mathematically, is that there is no rigid theoretical ground for model II. Secondary, the error - difference between experiment and model II prediction - becomes larger as the PhOH concentration in external phase goes lower. When the concentration of PhOH is lower than 0.01N, the error is unbearable. This phenomenon probably is because that chemical equilibrium has not achieved and/or the concentration of phenol oxide in the membrane phase has become important. The last one can be partially solved by letting equilibrium constant K to be an adjustable parameter.

In the future, the study of the optimum operating conditions is suggested by the author. Of course, this makes the relative simple and accurate Model II proposed here more attractive.

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