SIMULATION OF PARTICLE SIZE DISTRIBUTION IN CONTINUOUS EMULSION POLYMERIZATION THROUGH A MODIFIED POPULATION BALANCE APPROACH

by

Ying-Yuh Lu

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Name of Candidate: Ying-Yuh Lu
Master of Science in Chemical Engineering,
1984

Thesis and Abstract Approved: ______________________ ________
Dr. Chen-Chong Lin Date
Division of Chemical Engineering

Signatures of other members
of the thesis committee ______________________ ________
Date

______________________ ________
Date

VITA

Name: Ying-Yuh Lu

Degree and date to be conferred: Master of Science, 1984

Secondary education: ChaiYi High School, 1974

Collegiate institutions attended	Dates	Degree	Date of Degree
Tatung Institute of Technology	1974	B.S.	June, 1978
New Jersey Institute of Tech.	1982	M.S.	Oct. 1984

Major: Chemical Engineering

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ABSTRACT

Title of Thesis

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Ying-Yuh Lu
Master of Science in Chemical Engineering, 1984

Thesis directed by
Dr. Chen-Chong Lin
Division of Chemical Engineering Department

A detailed mathematical model for particle size distribution in continuous emulsion polymerization of styrene and vinyl acetate is proposed on the basis of the population balance in the presence of several kinetic and mass transfer processes. This study is limited to the Smith-Ewart case II, which assumes instantaneous free radical termination within polymer particles. Radical desorption mechanism from polymer particles is included in the model and the desorption rate is formulated from the diffusion theory which suggests that the rate coefficient should be inversely proportional to the surface area of polymer particles.

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CHAPTER 1

INTRODUCTION

Emulsion polymerization in both batch and continuous reactors is a major processing step in the manufacture of polymer products such as paints, inks, coatings, adhesives, high-impact strength copolymers, etc. Current production by emulsion polymerization in the United States is on the order of ten billion pounds per year. In spite of this great economic importance, the detailed mechanistic and quantitative behavior of these reactors is not well understood. Most early workers in the field chose to use batch reactor equipment to investigate emulsion polymerization kinetics. Small scale equipment and minimum reagent requirements led quite naturally to the use of batch studies. Batch reactors, however, tend to be time variant, i.e. transient phenomena are introduced. Continuous emulsion polymerizers may be operated at a truly "steady state" condition, thereby allowing easier analysis of the process. In addition, as more and more industrial processes become continuous, a complete analysis of emulsion polymerization becomes more important. For this reason, there is a great deal of interest in developing reliable, predictive mathematical models for continuous emulsion polymerization reactors.

The emulsion polymerization systems are thought to be a dispersion of soap micelles, polymer particles and monomer droplets in an aqueous medium. The conceptual picture of emulsion polymerization was first set down by Harkins(1) in 1947. He suggested that the micelle, swollen with monomer, serves as a locus for particle nucleation and subsequent growth. The micelle also contributes soap to help stabilize the growing polymer particles in later stages of growth. If a micelle fails to give birth to a polymer particle, the micelle is eventually adsorbed by other growing particles. The monomer droplets serve as reserviors and supply monomer by diffusion to growing particles. Smith and Ewart(2) then developed a mathematical description of Harkins' conceptual picture. They developed a steady state recursion relation which described the transfer of free radicals between the water phase and the polymer particles. Their recursion relation allowed for radicals to be absorbed by polymer particles to initiate polymer growth, terminate within the particles, and desorb from the polymer particles. Smith and Ewart solved their recursion relation for several limiting cases. The limiting case most widely discussed is their case II kinetics wherein the rate of termination of free radicals in the particles is assumed infinitely fast and the desorption mechanism is assumed inoperative. A consequence of these assumptions is that the average number of free radicals per polymer particle,

$\bar{n}_s$, is 0.5 for the system. That is, at any time, half of the particles present have one radical and are in a growing state, while the other half are inactive. Stockmayer(3) was able to analytically solve the steady state Smith-Ewart recursion relation by employing a generating function, but erred in that part of the solution which involves desorption. O'Toole(4) corrected the error and presented a general solution. Ugelstad et al.(5) realized that the rate of absorption of free radicals should be affected by the rate of desorption of free radicals from polymer particles. They included this effect and presented the results of a numerical solution to the steady state recursion relation. Gardon(6) maintained the time derivative term in his solution to the recursion relation, realizing full well that a batch reactor is never at "steady state". That his results deviated minimally from those of Stockmayer(3) is evidence that the "constant rate" time period may be adequately approximated by the steady state solution. Sundberg(7) showed that the population balance approach may be used to model batch emulsion polymerization processes. His model determined transient particle size distributions where the desorption mechanism was ignored. He was also able to predict molecular weight distributions from his model.

Continuous stirred tank reactors typically have inherent advantages for large scale commercial productions. The first significant discussion of continuous emulsion polymerization was presented by Gershberg and Longfield(8) in 1961. Their model assumed Smith-Ewart case II kinetics and ignored particle size distributions. Sato and Taniyama(9), Omi(10) and Nomura(11) did many works on the kinetic study for continuous process,too. The total particle concentration, conversion and molecular weight of a CSTR product were predicted from their model, but in all of these works the consideration of particle size distribution was neglected. In 1971, DeGraff and Poehlein(12) tried to predict the latex particle size distribution concerned with residence time distribution in CSTR without considering the radical desorption from polymer particles. They found that the latex particle size distribution in the product of a CSTR is quite different from that of a batch reactor product. In 1972, Stevens and Funderburk(13) first developed the prediction of particle size distribution by using the population balance approach, but the radical desorption process was not included. In 1974, Min and Ray(14) proposed the most general and extensive model, which consists of complex multivariate population balance equations coupled to material and energy balances for the reactor. However, they did not show any quantitative results generated from their equations. In 1977, Thompson and Stevens(15) reused the population balance method to formulate the particle size distribution with radical desorption and finite termination rate, in which a modified Smith-Ewart recursion relation was incorporated directly as the "rate of formation" relation for polymer particles.

Then, in 1978, Cauley, Giglio and Thompson$^{(16)}$ assumed instantaneous termination between two radicals over the entire reaction to simplify the Stevens' model.$^{(15)}$ However, no absolute number of polymer particles could be obtained by their model, unless the valus of N_{To}, the number density of polymer particles at size of micelle, is known for a given system. In this work, we modified Thompson and his coworkers' work by using the mass balance equation of the total polymer particles of CSTR as the boundary condition of the differential equations in the model. And the radical desorption process is formulated on the basis of diffusion theory. Therefore, the absolute particle size distribution and total concentration of polymer particles can be found. The effects of mean residence time, initiator level, emulsifier level and radical desorption process on the conversion, particle size distribution and total concentration of polymer particles in the product of CSTR are predicted. The experimental data for styrene system done by Nomura et al.$^{(11)}$ and for vinylacetate system done by Lu et al.$^{(17)}$ are given for comparision.

CHAPTER II

THEORETICAL CONSIDERATION

A. Assumptions

The heterogeneous nature of the latex system makes it necessary to consider a fairly large number of assumptions even for the simplest model. Most of these result from the utilization of Harkin's mechanism and the Smith-Ewart case II to describe the process. The present discussion is limited as follows:

(1) Reaction is carried out under steady state in a CSTR.

(2) Monomer concentration in polymer particles keeps constant no matter what concentration of initiator or emulsifier is fed into the reaction system.

(3) Termination reaction between two radicals is instantaneously occurred.

(4) The radical desorption from polymer particles is possible.

(5) There is no coalescence or breakage among particles.

(6) The reentry of radicals coming from the desorption process into particles is neglected.

(7) A feed stream contains no polymer particles.

(8) Monomer and polymer are mutually soluble.

(9) The polymer particles formed in water phase are ignored.

B. Definitions

1. Number density, $\hat{N}_i(r^3,t)$

To predict the particle size distribution in continuous emulsion polymerization, we define $\hat{N}_i(r^3,t)$ as the number density of polymer particles with i free radicals. The unit of $\hat{N}_i(r^3,t)$ is (moles of particles)/(1-H_2O)·(cm^3).

$$\int_x^y \hat{N}_i(r^3,t)d(r^3) \equiv \text{Total number of polymer particles between sizes x and y which contain i radicals.}$$

2. Total number density, $\hat{N}(r^3,t)$

The assumption of instantaneous termination within polymer particles stipulates that only $\hat{N}_o$ and $\hat{N}_1$ type particles exist in the system.

$$\hat{N}(r^3,t) = \sum_{i=1}^{n} \hat{N}_i(r^3,t) = \hat{N}_o(r^3,t) + \hat{N}_1(r^3,t) \qquad (1)$$

3. The concentration of total polymer particles, $\hat{N}_T$, (moles of particles/1-H_2O)

$$\hat{N}_T = \int_{r_m^3}^{\infty} \hat{N}(r^3,t)d(r^3) \qquad (2)$$

where r_m is the radius of the micelle, (cm)

4. The total surface area of polymer particles (per liter of water), $\hat{A}_p$ $(cm^2/1\text{-}H_2O)$

$$\hat{A}_p = 4\pi N_{av} \int_{r_m^3}^{\infty} r^2 \hat{N}(r^3,t)\,d(r^3) \qquad (3)$$

where N_{av} is Avogadros' number.

5. The total surface area of the micelles plus the polymer particles (per liter of water), $\hat{A}_s$ $(cm^2/1\text{-}H_2O)$

$$\hat{A}_s = 4\pi r_m^2 N_{av} m + \hat{A}_p \qquad (4)$$

where m is the concentration of micelles, $(moles/1\text{-}H_2O)$. As long as any micelles remain in the system, the total surface area must be constant and equal to that provided by the initial micelle surface. Thus,

$$\hat{A}_s = 4\pi r_m^2 N_{av} m_o \qquad (5)$$

where m_o is the initial concentration of micelles, $(moles/1\text{-}H_2O)$.

C. Model Development

Before going to set up the population balance equation, we should recognize the volumetric growth rate of polymer particles, free radical absorption rate and free radical desorption rate.

1. The rate of volumetric growth of polymer particle, $d(r^3)/dt$.

   The polymer particle volumetric growth rate has been developed by Gardon$^{(18)}$ as

   $$\frac{d(r^3)}{dt} = K\,i \tag{6}$$

   where

   $$K = \left(\frac{3}{4\pi}\right)\cdot\left(\frac{k_p}{N_{av}}\right)\cdot\left(\frac{\rho_m}{\rho_p}\right)\cdot\left(\frac{\phi_M}{1-\phi_M}\right) \times 10^3 \tag{7}$$

   and i = number of radicals in a growing particle . Here k_p is propagation rate constant, ρ_m and ρ_p are the densities of monomer and polymer, ϕ_M is the volume fraction of monomer in the polymer particle, and 10^3 is simply the conversion factor between cm^3 and liters (required when k_p is expressed in liters and r in cm). The unit of K is (1/hr).

   In this model, i is only 0 or 1. Therefore, the volumetric growth rate of $\hat{N}_0$ type particles, called dead polymer particles, becomes zero. And the volumetric growth rate of $\hat{N}_1$ type particles, called growing polymer particles, becomes K. Hence, the rate at which particles grow past size r^3 may be written as

$$H(r^3,t) = \hat{N}_1(r^3,t) \cdot \frac{d(r^3)}{dt} = K\hat{N}_1(r^3,t) \tag{8}$$

2. The rate of polymer particle absorption of a free radical from the aqueous phase

Owing to the fact that the rate of radical capture of the polymer particles is proportional to the fraction of the total surface area represented by a given particle type$^{(18)}$, the rate at which $\hat{N}_1$ type particles shifts population due to absorbance of a free radical from the aqueous phase in size x to y is :

$$E_1 = R\frac{4\pi N_{av}}{\hat{A}_s}\int_x^y r^2[\hat{N}_o(r^3,t)-\hat{N}_1(r^3,t)]\,d(r^3) \tag{9}$$

The rate at which $\hat{N}_o$ type particles shifts population due to absorbance of a free radical from the aqueous phase in size x to y is :

$$E_o = R\frac{4\pi N_{av}}{\hat{A}_s}\int_x^y r^2[\hat{N}_1(r^3,t)-\hat{N}_o(r^3,t)]\,d(r^3) \tag{10}$$

where

R is the formation rate of initiator radicals, (moles/l-hr). For steady state CSTR,

$$R = 2fk_d[I] = 2fk_d\frac{[I_f]}{1+k_d\hat{\theta}} \tag{11}$$

3. The rate of radical desorption from polymer particles

Referring to the radical desorption mechanism, early investigators(2) suggested the radical desorption rate is inversely proportional to the particle radius. According to the diffusion theory, researchers(19,20,21) recently have found that the radical desorption rate should be inversely proportional to the surface area of polymer particles. We take the latter concept in this model development. The radical desorption rate, k_f, is defined as:

$$k_f = \frac{D_o}{r^2} \tag{12}$$

where D_o is a Pseudo-desorption-coefficient, (cm^2/hr).

Hence, the rate at which $\hat{N}_1$ type particles shift population due to desorption of a free radical in size x to y is :

$$G_1 = -\int_x^y \frac{D_o}{r^2} \hat{N}_1(r^3,t)\, d(r^3) \tag{13}$$

The rate at which $\hat{N}_o$ type particles shift population due to desorption of a free radical in size x to y is :

$$G_o = + \int_x^y \frac{D_o}{r^2} \hat{N}_1(r^3,t)\, d(r^3) \tag{14}$$

4. The population balance equations

In this model, the population balances must be written for the growing and dead polymer particles. Following Behnken et al.$^{(22)}$,

For growing polymer particles:

$$\begin{bmatrix}\text{Rate of change in}\\ \text{the number of}\\ \text{growing polymer}\\ \text{particles in size}\\ \text{range x to y}\end{bmatrix} = \begin{bmatrix}\text{Rate at which}\\ \text{growing polymer}\\ \text{particles flow}\\ \text{into reactor in}\\ \text{size range x to y}\end{bmatrix} - \begin{bmatrix}\text{Rate at which}\\ \text{growing polymer}\\ \text{particles flow}\\ \text{out reactor in}\\ \text{size range x to y}\end{bmatrix}$$

$$+ \begin{bmatrix}\text{Rate at which}\\ \text{growing polymer}\\ \text{particles grow}\\ \text{into size at x}\end{bmatrix} - \begin{bmatrix}\text{Rate at which}\\ \text{growing polymer}\\ \text{particles grow}\\ \text{out of size at y}\end{bmatrix}$$

$$+ \begin{bmatrix}\text{Rate at which growing polymer par-}\\ \text{ticles shift population dut to ab-}\\ \text{sorbance of a free radical from the}\\ \text{aqueous phase in size range x to y}\end{bmatrix}$$

$$+\left[\begin{array}{l}\text{Rate at which growing polymer par-}\\ \text{ticles shift population due to de-}\\ \text{sorption of a free radical in size}\\ \text{range x to y}\end{array}\right]$$

In the nomenclature set forth here, for particles containing one radical, $\hat{N}_1(r^3,t)$, this balance becomes

$$\frac{\partial}{\partial t}\int_x^y \hat{N}_1(r^3,t)\,d(r^3) = \frac{1}{\hat{\theta}}\int_x^y \hat{N}_{1f}(r^3,t)\,d(r^3) - \frac{1}{\hat{\theta}}\int_x^y \hat{N}_1(r^3,t)\,d(r^3) + H(x,t) - H(y,t) + E_1 + G_1 \qquad (15)$$

From eqn.(8), we know

$$H(x,t) - H(y,t) = -\int_x^y \frac{\partial(K\hat{N}_1(r^3,t))}{\partial(r^3)}\,d(r^3) \qquad (16)$$

Substituting eqns.(9), (13), (16) into eqn.(15), the eqn.(15) becomes

$$\int_x^y \left\{ \frac{\partial \hat{N}_1(r^3,t)}{\partial t} - \frac{\hat{N}_{1f}(r^3,t)-\hat{N}_1(r^3,t)}{\hat{\theta}} + K\frac{\partial \hat{N}_1(r^3,t)}{\partial(r^3)} - R\frac{4\pi N_{av}}{\hat{A}_s} r^2 (\hat{N}_o(r^3,t) - \hat{N}_1(r^3,t)) + \frac{D_o}{r^2}\hat{N}_1(r^3,t)\right\} d(r^3)=0 \quad (17)$$

Since the integrand vanishes for an arbitrary size interval (x,y), it must be identically zero, leading to

$$\frac{\partial \hat{N}_1(r^3,t)}{\partial t} = \frac{\hat{N}_{1f}(r^3,t)-\hat{N}_1(r^3,t)}{\hat{\theta}} - K\frac{\partial \hat{N}_1(r^3,t)}{\partial (r^3)} + R\frac{4\pi N_{av}}{\hat{A}_s} r^2(\hat{N}_o(r^3,t) - \hat{N}_1(r^3,t)) - \frac{D_o}{r^2}\hat{N}_1(r^3,t) \qquad (18)$$

A similiar analysis for the dead polymer particles leads to

$$\frac{\partial \hat{N}_o(r^3,t)}{\partial t} = \frac{\hat{N}_{of}(r^3,t)-\hat{N}_o(r^3,t)}{\hat{\theta}} + R\frac{4\pi N_{av}}{\hat{A}_s} r^2(\hat{N}_1(r^3,t) - \hat{N}_o(r^3,t)) + \frac{D_o}{r^2}\hat{N}_1(r^3,t) \qquad (19)$$

where there is no partial derivative with respect to (r^3) because dead polymer particles can not grow until they become active. Implicit in the growing polymer particles relationship is the assumption that the volume fraction of monomer ϕ_M is not a function of particle size in the range of interest.(23)

Under the assumptions of steady state in a CSTR and no polymer particle in feed, the population balance equations,(18) and (19), become

$$K\frac{d\hat{N}_1(r^3)}{d(r^3)} = R\frac{4\pi N_{av}}{\hat{A}_s}r^2(\hat{N}_o(r^3) - \hat{N}_1(r^3)) - \frac{1}{\hat{\theta}}\hat{N}_1(r^3) - \frac{D_o}{r^2}\hat{N}_1(r^3) \qquad (20)$$

$$0 = R\frac{4\pi N_{av}}{\hat{A}_s}\,r^2(\hat{N}_1(r^3) - \hat{N}_o(r^3)) - \frac{1}{\hat{\theta}}\hat{N}_o(r^3) + \frac{D_o}{r^2}\hat{N}_1(r^3) \qquad (21)$$

5. The boundary condition

Only one boundary condition is needed to solve eqn. (20). We make the following overall material balance for the total polymer particles as the boundary condition.

$$\frac{d\hat{N}_T}{dt} = \eta R(1 - \frac{\hat{A}_p}{\hat{A}_s}) + \frac{1}{\hat{\theta}}(\hat{N}_{Tf} - \hat{N}_T) \qquad (22)$$

where η is a surface affinity factor to account for the relative ease of radicals entry into micelles versus particles.(24) Only radicals captured by the micelles are capable of creating new particles. And the rate of nucleation of new particles is proportional to the total surface area of micelles.(18) Eqn.(22) indicates the rate of change in the total polymer particles in a CSTR. Then, under the assumptions of steady state and no polymer particles in feed, the eqn.(22) becomes eqn.(23).

$$\hat{N}_T = \eta R \hat{\theta} \left(1 - \frac{\hat{A}_p}{\hat{A}_s}\right) \tag{23}$$

Coupling with the definitions of $\hat{N}_T$ and $\hat{A}_p$, eqn.(23) can be rewritten as eqn.(24).

$$\int_{r_m^3}^{\infty} \hat{N}\, d(r^3) = \eta R \hat{\theta} \left\{ 1 - \frac{4\pi N_{av}}{\hat{A}_s} \int_{r_m^3}^{\infty} r^2 \hat{N}\, d(r^3) \right\} \tag{24}$$

Rearranging eqn.(24) obtains eqn.(25).

$$\eta R\hat{\theta} = \int_{r_m^3}^{\infty} (\eta R \hat{\theta} \frac{4\pi N_{av}}{\hat{A}_s} r^2 + 1) \hat{N}\, d(r^3) \tag{25}$$

Now, eqn.(25) is our boundary condition.

6. The dimensionless forms of the population balance equations

For mathematical convenience, the eqns.(20), (21), (1) and (25) are now expressed in dimensionless forms and rearranged as eqns.(26), (27), (28) and (29), respectively.

$$\frac{dN_1}{d\upsilon^3} + (\gamma + \beta\upsilon^{-2} + \alpha\upsilon^2)N_1 - \alpha\upsilon^2 N_o = 0 \tag{26}$$

$$N_o = \frac{\beta\upsilon^{-2} + \alpha\upsilon^2}{\gamma + \alpha\upsilon^2} N_1 \tag{27}$$

$$N = N_o + N_1 = \frac{\gamma + \beta\upsilon^{-2} + 2\alpha\upsilon^2}{\gamma + \alpha\upsilon^2} N_1 \tag{28}$$

$$\eta\alpha = \int_1^{\infty} (\gamma + \frac{\eta\alpha\upsilon^2}{A_s}) N d(\upsilon^3) \tag{29}$$

All the dimensionless groups presented in the eqns. (26) - (29), such as N_o, N_1, α, β, etc., are defined in Table 1.

Table 1 The Dimensionless Groups in The Population Balance Equations

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$$N_i = \frac{r_m^3 \hat{N}_i}{m_o} = \text{dimensionless particle number density}$$

$$A_s = \frac{\hat{A}_s}{4\pi r_m^2 N_{av} m_o} = \text{dimensionless total surface area}$$

$$\nu = \frac{r}{r_m} = \text{dimensionless particle radius}$$

$$\alpha = \frac{R r_m^3}{K m_o} = \frac{\text{radical absorption rate}}{\text{particle growth rate}}$$

$$\beta = \frac{r_m D_o}{K} = \frac{\text{radical desorption rate}}{\text{particle growth rate}}$$

$$\gamma = \frac{r_m^3}{K\hat{\theta}} = \frac{\text{space velocity}}{\text{particle growth rate}}$$

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7. The particle size distribution functions

After substituting eqn.(27) into eqn.(26), the solution of eqn.(26) leads to the dimensionless particle size distribution function $N_1(\upsilon^3)$,

$$N_1(\upsilon^3) = N_1(1)\,\exp(\,F(\upsilon^3)\,) \tag{30}$$

where

$$F(\upsilon^3) = -2\gamma(\upsilon^3 - 1) + \frac{3\gamma^2}{\alpha}(\upsilon - 1) - 3\left(\frac{\gamma^{5/2}}{\alpha^{3/2}} + \beta\frac{\gamma^{1/2}}{\alpha^{1/2}}\right)\cdot \tan^{-1}\left(\frac{\sqrt{\frac{\alpha}{\gamma}}\,(\upsilon - 1)}{1 + \frac{\alpha}{\gamma}\upsilon}\right) \tag{31}$$

The detailed solution is shown in the Appendix A. Now, only an integration constant , $N_1(1)$, the dimensionless number density of active polymer particles at $\upsilon = 1$, is necessary to be solved. By substituting eqn.(28) and eqn.(30) into the boundary condition of eqn.(29), the result gives

$$N_1(1) = \eta\alpha\left\{\int_1^{\infty}(\gamma + \eta\alpha\upsilon^2)\left(\frac{\gamma + \beta\upsilon^{-2} + 2\alpha\upsilon^2}{\gamma + \alpha\upsilon^2}\right)\cdot \exp(\,F(\upsilon^3)\,)\,d(\upsilon^3)\right\}^{-1} \tag{32}$$

Then, the dimensionless particle size distribution functions, $N_1(\upsilon^3)$, $N_o(\upsilon^3)$ and $N(\upsilon^3)$, can be obtained through the computation of eqns.(30), (27) and (28), respectively.

Transfering each dimensionless groups into dimensional parameters by setting r_m and m_o as

$$r_m = \left(\frac{Em \cdot a}{4\pi} \right)^{1/2}$$

$$m_o = \frac{[S_f] - [CMC]}{E_m}$$

where

Em is the number of emulsifier molecules per micelle,

a is the area occupied by single emulsifier molecule, and

[CMC] is criticle micelle concentration,(mole/l-H_2O).

According to the literature$^{(29)}$, the number of emulsifier molecules per micelle ranging from 50 to 100 may be used to calculate the micellar radius (r_m) and the concentration of micelles (m_o). A series of preliminary calculations were done for several values of Em in the range from 50 to 300. The results obtained by these computations did not exhibit large variation for the case of styrene polymerization. Therefore, the number of emulsifier molecules per micelle, Em , is chosen to be 100 in this study. The feed concentration of micelles (m_o) is then approximated as

$$m_o = \frac{[S_f] - [CMC]}{100}$$

and the radius of micelle is calculated as

$$r_m = \left(\frac{100\ a}{4\ \pi} \right)^{1/2}$$

Hence, the dimensional particle size distribution functions $\hat{N}_1(r^3)$, $\hat{N}_o(r^3)$ and $\hat{N}(r^3)$ are obtained. Meanwhile, the total polymer particle concentration ($\hat{N}_T$), conversion (X), average radii of polymer particle ($\bar{r}_n$ or $\bar{r}_w$), system average number of radicals per polymer particle ($\bar{n}_s$) and polydispersity of radius for polymer particle size distribution (P) can also be found from the following equations, respectively,

$$\hat{N}_T = \int_{r_m^3}^{\infty} \hat{N}(r^3)\ d(r^3) \tag{33}$$

$$X = k_p \frac{[M_p]}{[M_f]} \hat{\theta} \int_{r_m^3}^{\infty} \hat{N}_1(r^3)\ d(r^3) \tag{34}$$

$$\bar{r}_n = \frac{\int_{r_m^3}^{\infty} r\ \hat{N}(r^3)\ d(r^3)}{\int_{r_m^3}^{\infty} \hat{N}(r^3)\ d(r^3)} \tag{35}$$

$$\bar{r}_w = \frac{\int_{r_m^3}^{\infty} r^4 \hat{N}(r^3)\, d(r^3)}{\int_{r_m^3}^{\infty} r^3 \hat{N}(r^3)\, d(r^3)} \qquad (36)$$

$$\bar{n}_s = \frac{\int_{r_m^3}^{\infty} \hat{N}_1(r^3)\, d(r^3)}{\int_{r_m^3}^{\infty} \hat{N}(r^3)\, d(r^3)} \qquad (37)$$

$$\bar{n} = \frac{\hat{N}_1(r^3)}{\hat{N}(r^3)} \qquad (38)$$

$$P = \frac{\bar{r}_w}{\bar{r}_n} \qquad (39)$$

CHAPTER III

SIMULATION OF PARTICLE SIZE DISTRIBUTION IN CONTINUOUS EMULSION POLYMERIZATION OF STYRENE

A. Experimental condition and physical constants

The polymerization condition and physical constants in continuous emulsion polymerization of styrene used for the calculation of this model are mostly based on Nomura's work(11) and given in Table 2. Among the polymerization studies of styrene, some of works neglected the radical desorption mechanism, but some of works emphasized the importance of the radical desorption mechanism. From all of these research works, it has been known that the radical desorption mechanism may or may not be significant, depending on the polymerization conditions. In the present work, the assumption of no radical desorption from the polymer particles is made, i.e. $D_o = 0.0$ in this model, during the polymerization of styrene.

Table 2 Experimental Condition(11) and Physical Constants in Continuous Emulsion Polymerization of Styrene

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$T = 50^{o}C$

$[M_p] = 5.48$ (mole/l)

$[I_f] = 4.6296 \times 10^{-3}$ (mole/l-H_2O)

$[M_f]$ = 4.8077 (mole/1-H_2O)
$[S_f]$ = 0.0434 (mole/1-H_2O)
k_p = 7.632×10^5 (1/mole-hr)
k_d = 3.64×10^{-3} (hr^{-1})
$k_d f$ = 2.394×10^{-3} (hr^{-3})
a = 3.5×10^{-15} (cm^2/molecule)
ρ_p = 1.0 (g/cm^3)
ρ_m = 0.903 (g/cm^3)
ϕ_M = 0.6(6)
η = 0.4(24)

B. Results and discussion

1. Particle size distribution

Fig.1 shows the relationship between the dimensional particle size distribution and mean residence time. It is found that particle size distribution curves will become wider and shift into larger particle size region at longer mean residence time. This indicates that polymer particles will grow into larger sizes at longer mean residence time. The effects of the level of emulsifier and initiator, $[S_f]$ and $[I_f]$, on particle size distribution are given in figure 2 and 3, respectively. The height of particle size distribution curves becomes higher with increasing the value of $[S_f]$, but the shapes of these curves remain almost the same as shown in Fig. 2. This means that the concentration of emulsifier in feed does not affect the polydispersity of radius $(\bar{r}_w/\bar{r}_n)$, which is often used to indicate the breadth of the distribution. Little effect on the particle size distribution can be found by altering the level of initiator, $[I_f]$, as shown in Fig. 3.

2. The concentration of total polymer particles

Fig.4 shows the plot of total concentration of polymer particles, $\hat{N}_T$, versus mean residence time, $\hat{\theta}$, in which the effect of η on $\hat{N}_T$ is also given for comparison. The dotted line is the case for $\eta = 1$, while the solid line is the case for $\eta = 0.4$(24), and the circles in the figure are the experimental data obtained from Nomura et al. It is found that the factor η contributes a more significant effect on $\hat{N}_T$ at small mean residence times, and the solid line fits the experimental data better. The surfaces of micelles and polymer particles have a different efficiency for capturing the initiator radicals, and η is the correction constant which is experimentally determined by curve fitting the experimental data to be $\eta = 0.4$(24). It is seen that the effect of η is more significant at the shorter mean residence time. Figs. 5 and 6 show the effects of the level of emulsifier and initiator, $[S_f]$ and $[I_f]$, on the total concentration of polymer particle, $\hat{N}_T$, versus mean residence time, respectively. As shown in these figures, $\hat{N}_T$ will increase with increasing the value of $[S_f]$ because larger total micelle surface area can generate more polymer particles. The effect of $[I_f]$ becomes more significant at shorter mean residence time but becomes less significant at longer mean residence time. The reason is that if the mean residence time is small, particle nucleation will be limited by radical initiation. Thus, a higher level of $[I_f]$ can generate more polymer particles at small mean residence times. If the mean residence time is large, the controlling factor of polymer particle nucleation will be the concentration of micelles left in the system so that the levels of $[I_f]$ become insensitive on the $\hat{N}_T$ at larger mean residence times.

3. The system average number of radicals per polymer particle

A plot of system average number of radicals per polymer particle, $\bar{n}_s$, versus mean residence time is shown in Fig.7. No effect can be found by altering

η in this case. The value of $\bar{n}_s$ approaches 0.5 when $\hat{\theta}$ becomes longer. This situation coincides with Smith-Ewart case II. The reason is that just after the start of the reaction there are very few particles but they all contain one radical because the free radicals generated in solution quickly take up residence in the polymer particles. The absorption of radicals is rapid relative to their generation. Much later there are many particles but on the average half of them contain a single radical and half contain none because the termination of two radicals is instantaneous. As the result, the system average number of radicals per polymer particle is 0.5. The levels of emulsifier and initiator give no significant effect on the system average number of radicals per polymer particle as shown in Fig.8 and Fig.9, respectively.

4. The conversion

Fig.10 shows the conversion, X, versus mean residence time. The solid line with $\eta = 0.4$ gives better agreement with experimental data than the dotted line with $\eta = 1$, and the influence of η becomes less significance at long mean residence times. The effect of the level of emulsifier on the conversion can be seen in Fig.11. The value of conversion will become greater with increasing the value of $[S_f]$ because the increase of $[S_f]$ will lead to increase in the total concentration of polymer particles, and the conversion is in proportion to the total concentration of polymer particles. Furthermore, the computation shows that the influence of the level of initiator, $[I_f]$, on conversion is very small as seen in Fig.12.

5. The number average radius and weight average radius

Fig.13 shows the number average radius and weight average radius of polymer particles as a function of mean residence time. As shown in this figure, larger particles will be formed in longer mean residence time. Fig.14 shows the polydispersity of radius, $\bar{r}_w/\bar{r}_n$, vs. mean residence time, indicating the effect of mean residence time on the breadth of distribution as seen in Fig.1. The value of polydispersity of radius will increase with increasing the mean residence time. It is further found through simulation that the levels of emulsifier and initiator do not affect the polydispersity of radius.

C. Conclusion

The simulation based on the present model demonstrated the following features of continuous emulsion polymerization of styrene monomer which can provide insight into some of the engineering ramifications of such processes.

(1) Polymer particle size distribution curves will become wider and shift into larger particle size region at longer mean residence time.

(2) The effect of the levels of initiator and emulsifier on the particle size distribution are insignificant.

(3) The concentration of total polymer particles increases with increasing the level of emulsifier.

(4) The effect of the level of initiator on the concentration of total polymer particles is not significant especially at the long mean residence times in the case of CSTR.

(5) The value of conversion is an increasing function of the level of emulsifier. However, this quantity is practically invariant with respect to the level of initiator.

(6) The system average number of radicals per polymer particle, $\bar{n}_s$, approaches 0.5 at long mean residence time, which coincides with Smith-Ewart case II.

(7) The levels of emulsifier and initiator give less

important effect on the system average number of radicals per polymer particle.

CHAPTER IV

SIMULATION OF PARTICLE SIZE DISTRIBUTION IN CONTINUOUS EMULSION POLYMERIZATION OF VINYL ACETATE

In the literature it is generally concluded that the emulsion polymerization of vinyl acetate does not fall within the classic theories proposed by Smith-Ewart.(2) It is believed that this is due partly to the high transfer constant of monomer in vinyl acetate polymerization and partly to the relatively high solubility of vinyl acetate in water. In this model, we include a mechanism allowing radicals to escape from polymer particles.(25,26,27,28) This mechanism is necessary to explain the low concentration of radicals per polymer particle usually observed in vinyl acetate emulsion polymerization. The effect of radical desorption from polymer particles on particle size distribution, conversion, total concentration of polymer particles and concentration of radicals per polymer particle etc. will be discussed through the model proposed.

A. Experimental condition and physical constants

The polymerization condition and physical constants in continuous emulsion polymerization of vinyl acetate monomer used for the calculation of our model are mostly based on Lu's work(17) and given in Table 3.

Table 3 Experimental Condition(17) and Physical Constants in Continuous Emulsion Polymerization of Vinyl Acetate

$T = 50^{o}C$

$[M_p] = 8.95$ (mole/l-H_2O)

$[I_f] = 2.037X10^{-3}$ (mole/l-H_2O)

$[M_f] = 2.667$ (mole/l-H_2O)

$[S_f] = 0.01736$ (mole/l-H_2O)

$k_p = 1.188X10^{7}$ (l/mole-hr)

$k_d = 3.64X10^{-3}$ (hr^{-1})

$k_d f = 2.394X10^{-3}$ (hr^{-1})

$a = 3.5X10^{-15}$ (cm^2/molecule)

$\rho_p = 1.19$ (g/cm^3)

$\rho_m = 0.9335$ (g/cm^3)

$\phi_M = 0.8248$

$\eta = 1.0$

B.Results and discussion

1. Particle size distribution

The effect of free radical desorption on particle size distribution at $\hat{\theta}$ =0.5(hr) is shown in Fig.15. It is found that there is a large difference in particle size distribution curves between the cases with free radical desorption and without free radical desorption. The role of the radical desorption is to allow the free radicals, which are once trapped inside the polymer particles, to escape back into the water phase.
Owing to the fact that the free radical desorption rate is inversely proportional to the surface area of polymer particles$^{(20,25)}$, the free radicals inside polymer particles are easier to escape from the group of smaller polymer particles. As a result, the effect of the desorption is always very pronounced for the smaller size polymer particles. Thus, an occurrence of radical desorption from polymer particles will depress the growth of polymer particles and, in turn, broaden the particle size distribution, in which the system will contain more small size particles as seen in Fig.15.
Fig.16 is the plot of the particle size distribution against the different mean residence times at D_o = $0.19X10^{-7}(cm^2/hr)$. As one might expect, shorter mean

residence time yields products having more smaller polymer particles and fewer larger polymer particles. It is also seen that polymer particles will grow into larger sizes and broaden the particle size distribution at longer mean residence time. Fig.17 shows the effect of the level of emulsifier on the particle size distribution at $\hat{\theta} = 0.5$(hr) and $D_o = 0.19X10^{-7}$(cm^2/hr). As the level of emulsifier increase, more micelles become available for radical capture, which in turn produces more polymer particles in the system. But in this case , the ratio of the concentrations of free radicals to micelles becomes smaller, so that the growth of polymer particles will be depressed and the system will produce more small polymer particles. Fig.18 shows the effect of the level of initiator on the particle size distribution at $\hat{\theta} = 0.5$(hr) and $D_o = 0.19X10^{-7}$ (cm^2/hr). It is found that an increase in the level of initiator will yield more large polymer particles because more free radicals will be generated in the system to contribute to the radical absorption of polymer particles, which in turn increases the growth rate of polymer particles.

2. The concentration of total polymer particles

Fig.19 shows the effect of radical desorption on the concentration of total polymer particles vs. mean residence time. It is seen that an occurrence of free radical desorption process will increase the total concentration of polymer particles because the decrease in the total surface area of polymer particles due to the free radical desorption from polymer particles will cause more micelle formed in the system to generate more polymer particles. Fig.20 shows the effect of the level of emulsifier on total concentration of polymer particles vs. mean residence time. The concentration of total polymer particles will increase with increasing the level of emulsifier because more micelles become available for capturing the free radicals to generate new polymer particles. Fig.21 shows the effect of the level of initiator on the concentration of total polymer particles vs. mean residence time. As shown in this figure, the concentration of total polymer particles increases with increasing the level of initiator at small mean residence times, but at higher mean residence times, $\hat{\theta} > 0.3$(hr), the trends reverse. This is due to the fact that if the mean residence time is short, particle nucleation will be limited by free radical initiation. Thus, a higher level of initiator can generate more polymer particles at small mean residence times. If the mean residence time is large, the controlling step of polymer particle nucleation will be the concentration of micelles left in the system so that the increase of the level of initiator will decrease the concentration of total polymer particles.

3. System average number of radicals per polymer particle

Fig.22 shows the effect of radical desorption on system average number of radicals per polymer particle vs. mean residence time. If no radical desorption occurs during the polymerization of VAc system, the value of $\bar{n}_s$ approaches 0.5 because the termination of two radicals within polymer particles is instantaneous. But with the occurrence of radical desorption in the system, the value of $\bar{n}_s$ will be largely reduced to the order of 10^{-4}, because the radicals in residence, in this case, will be introduced back into the water phase, especially for the small size particles, thus shifting the equilibrium(i.e. lowering $\bar{n}_s$). The effects of the levels of emulsifier and initiator on system average number of radicals per polymer particle are plotted in Fig.23 and Fig.24, respectively. At lower level of emulsifier or higher level of initiator, the system is simply flooded with free radicals, generated from initiator molecules, to the extent that the mechanism of radical desorption from polymer particles is insignificant. The only meaningful mechanistic steps in this situation, therefore, are absorption and termination of radicals, where $\bar{n}_s$ increases. Fig. 25 shows the effect of radical desorption on average number of radicals per polymer particle vs. polymer particle size. It is found that the value of $\bar{n}$ is significantly decreased in the range of smaller particle sizes, but finally approaches 0.5 at the range of large sizes for the case of radical desorption system. This fact indicats the effect of radical desorption from polymer particles is more important at the smaller particle sizes.

4. Conversion

Fig.26 is the plot of the effect of radical desorption on conversion vs. mean residence time. Two circles in the figure is taken from the experimental data of Ref.(10). An increase in the magnitude of the radical desorption coefficient will significantly reduce the conversion. The evidence is more meaningful at shorter mean residence time because the conversion is entirely related to the system average number of radicals per polymer particle, $\bar{n}_s$, and the concentration of total polymer particles, $\hat{N}_T$. When the process of radical desorption from polymer particles occurs during the polymerization reaction, the decrease of system average number of radicals per polymer particle, as seen in Fig.22, is somewhat more significant than the increase of total concentration of polymer particles, as seen in Fig.19. By fitting method, it is found that $D_o = 0.19X10^{-7}(cm^2/hr)$ is the most suitable value for the vinyl acetate system. This value is accepted for all calculation of VAc system in this paper.

It is well known that the VAc monomer dissolves with relatively high concentration in its polymer and water phase. Therefore, the separate monomer phase should be vanished at even very early stage of polymerization, say . about 10% conversion. This is the reason why the experimental data is better fitted before 10% conversion , as seen in Fig.26. The effects of the levels of emulsifier and initiator on conversion vs. mean residence time at $D_o= 0.19X10^{-7}(cm^2/hr)$ are shown in Fig.27 and Fig.28, respectively. It is found that the increase of the level of emulsifier concentration does not necessary to increase the value of conversion, but an increase in the level of initiator concentration will cause a higher value of conversion in vinyl acetate system. These results are totally different from the styrene system which shows the conversion is proportional to the level of emulsifier concentration and is insensitive to the level of initiator concentration. All of these effects are attributable to the changes in the value of $\bar{n}_s$ and $\hat{N}_T$.

5. Number average radius and weight average radius

Fig.29 shows the effect of radical desorption on number average radius, $\bar{r}_n$, and weight average radius, $\bar{r}_w$. As seen in this figure, an occurrence of radical desorption will decrease both number and weight average radii. The ratio of $\bar{r}_w/\bar{r}_n$, which is often used to indicate the breadth of the distribution, is greatly increased in the case of radical desorption system,i.e. vinyl acetate system, as seen in figure 30. This fact indicates that the particle size distribution will become wider when the process of radical desorption from polymer particles occurs. Fig.31 and Fig.32 show the effects of the levels of initiator and emulsifier on number and weight average radii at $\hat{\theta} = 0.5(\text{hr})$ and $D_o = 0.19\text{X}10^{-7}(\text{cm}^2/\text{hr})$. It is found that the increase of the level of initiator will increase the magnitude of $\bar{r}_n$ and $\bar{r}_w$, while the increase of the level of emulsifier leads to the decrease of the magnitude of

$\bar{r}_n$ and $\bar{r}_w$. All of these effects are attributable to the change of $\bar{n}_s$.

C. Conclusion

The effect of radical desorption on continuous emulsion polymerization of vinyl acetate was studied through the model proposed. The simulation demonstrated the following features of VAc emulsion polymerization.

(1) The Pseudo-desorption-coefficient, D_o, for vinyl acetate system is best chosen as $0.19\text{X}10^{-7}(\text{cm}^2/\text{hr})$.

(2) The radical desorption from polymer particle depresses the growth rate of polymer particles and, in turn, broaden the particle size distribution in which the system produces more small polymer particles.

(3) The concentration of total polymer particles will increase with the occurrence of radical desorption.

(4) An increase in the magnitude of radical desorption mechanism can significantly reduce conversion.

(5) The higher the level of initiator, the greater will be the conversion , while the increase of the level of emulsifier does not necessarily increase conversion.

(6) The effect of radical desorption is more improtant at the smaller particle sizes.

(7) The value of $\bar{n}_s$ approaches 0.5 in the case of non-radical-desorption system , whearas the value of $\bar{n}_s$ is of the order of 10^{-4} and gradually increases with increasing mean residence times in the case of radical-desorption system, i.e. vinyl acetate system.

APPENDIX A

THE DETAILED SOLUTION OF POPULATION BALANCE EQUATIONS

$$\frac{dN_1}{d\upsilon^3} + (\gamma + \beta\upsilon^{-2} + \alpha\upsilon^2)N_1 - \alpha\upsilon^2 N_o = 0 \quad \text{....................(i)}$$

$$N_o = \frac{\beta\upsilon^{-2} + \alpha\upsilon^2}{\gamma + \alpha\upsilon^2} N_1 \quad \text{.......................................(ii)}$$

Substituting eqn.(ii) into eqn.(i) obtains eqn.(iii).

$$\frac{dN_1}{d\upsilon^3} + \frac{\gamma^2 + 2\gamma\alpha\upsilon^2 + \gamma\beta\upsilon^{-2}}{\gamma + \alpha\upsilon^2} N_1 = 0 \quad \text{.....................(iii)}$$

Integrating eqn.(iii) yields:

$$\frac{N_1(\upsilon^3)}{N_1(1)} = \exp[F(\upsilon^3)] \text{.....................................(iv)}$$

Where

$$F(\upsilon^{3}) = -\int_{1}^{\upsilon^{3}} \frac{\gamma^{2} + 2\gamma\alpha\upsilon^{2} + \gamma\beta\upsilon^{-2}}{\gamma + \alpha\upsilon^{2}} \, d(\upsilon^{3})$$

$$= -\int_{1}^{\upsilon} \frac{\gamma^{2} + 2\gamma\alpha\upsilon^{2} + \gamma\beta\upsilon^{-2}}{\gamma + \alpha\upsilon^{2}} \cdot 3\upsilon^{2} \, d\upsilon$$

$$= -3\int^{\upsilon} \left(2\gamma\upsilon^{2} - \frac{\gamma^{2}}{\alpha} + \frac{\frac{\gamma^{2}}{\alpha} + \beta}{1 + \frac{\alpha}{\gamma}\upsilon^{2}}\right) d\upsilon$$

$$= -3\int_{1}^{\upsilon} \left[2\gamma\upsilon^{2} - \frac{\gamma^{2}}{\alpha} + \left(\frac{\gamma^{2}}{\alpha} + \beta\right) \cdot \sqrt{\frac{\gamma}{\alpha}} \cdot \frac{\sqrt{\frac{\alpha}{\gamma}}}{1 + \left(\sqrt{\frac{\alpha}{\gamma}}\,\upsilon\right)^{2}}\right] d\upsilon$$

$$= -2\gamma(\upsilon^{3} - 1) + 3\frac{\gamma^{2}}{\alpha}(\upsilon - 1) - \left[3\frac{\gamma^{5/2}}{\alpha^{3/2}} + 3\beta\frac{\gamma^{1/2}}{\alpha^{1/2}}\right] \cdot \tan^{-1}\left[\frac{\sqrt{\frac{\alpha}{\gamma}}\,(\upsilon - 1)}{1 + \frac{\alpha}{\gamma}\upsilon}\right] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(\mathrm{v})$$

APPENDIX B

THE FIGURES OF CONTINUOUS EMULSION POLYMERIZATION OF STYRENE

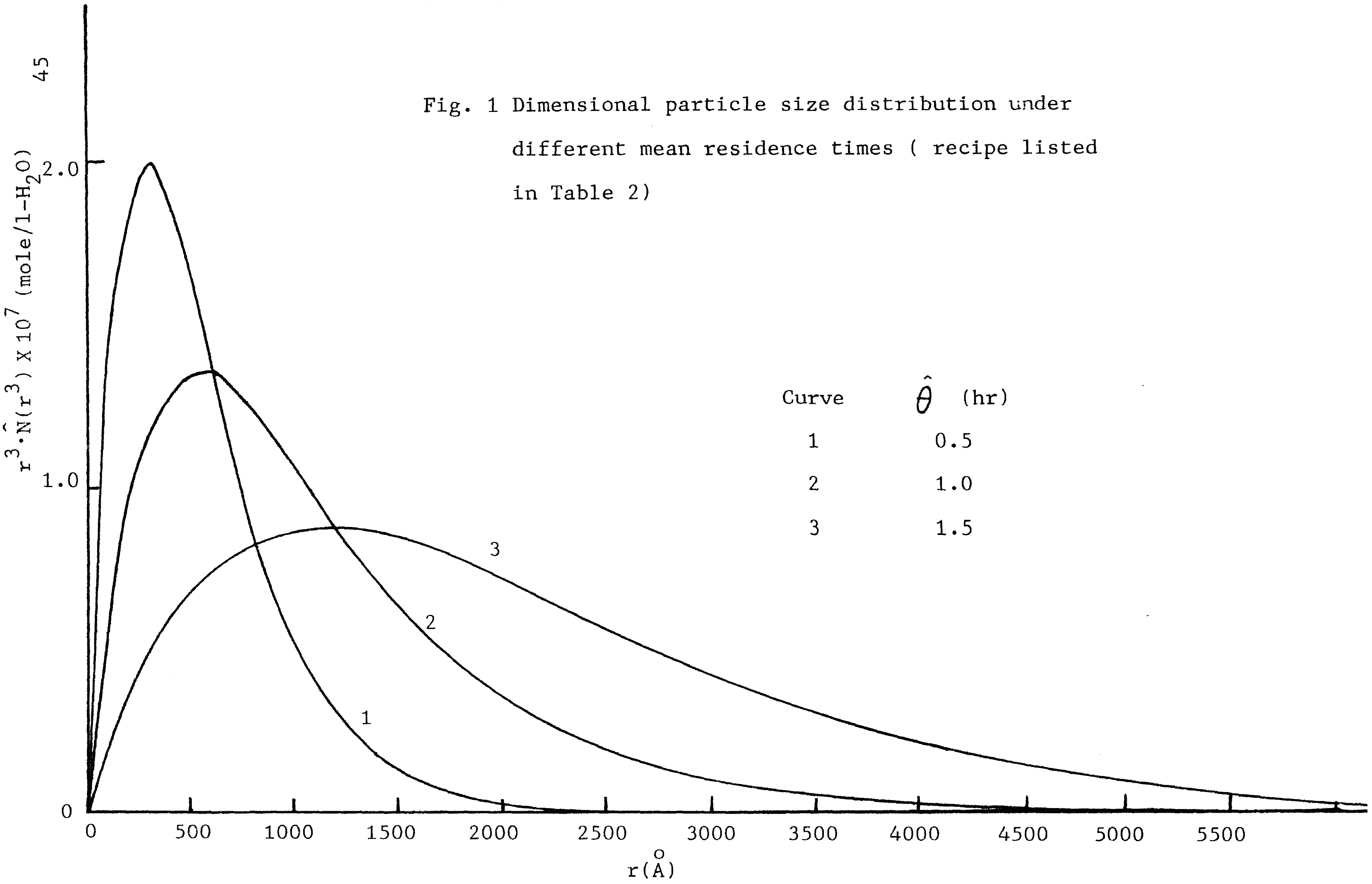


Fig. 1 Dimensional particle size distribution under different mean residence times (recipe listed in Table 2)

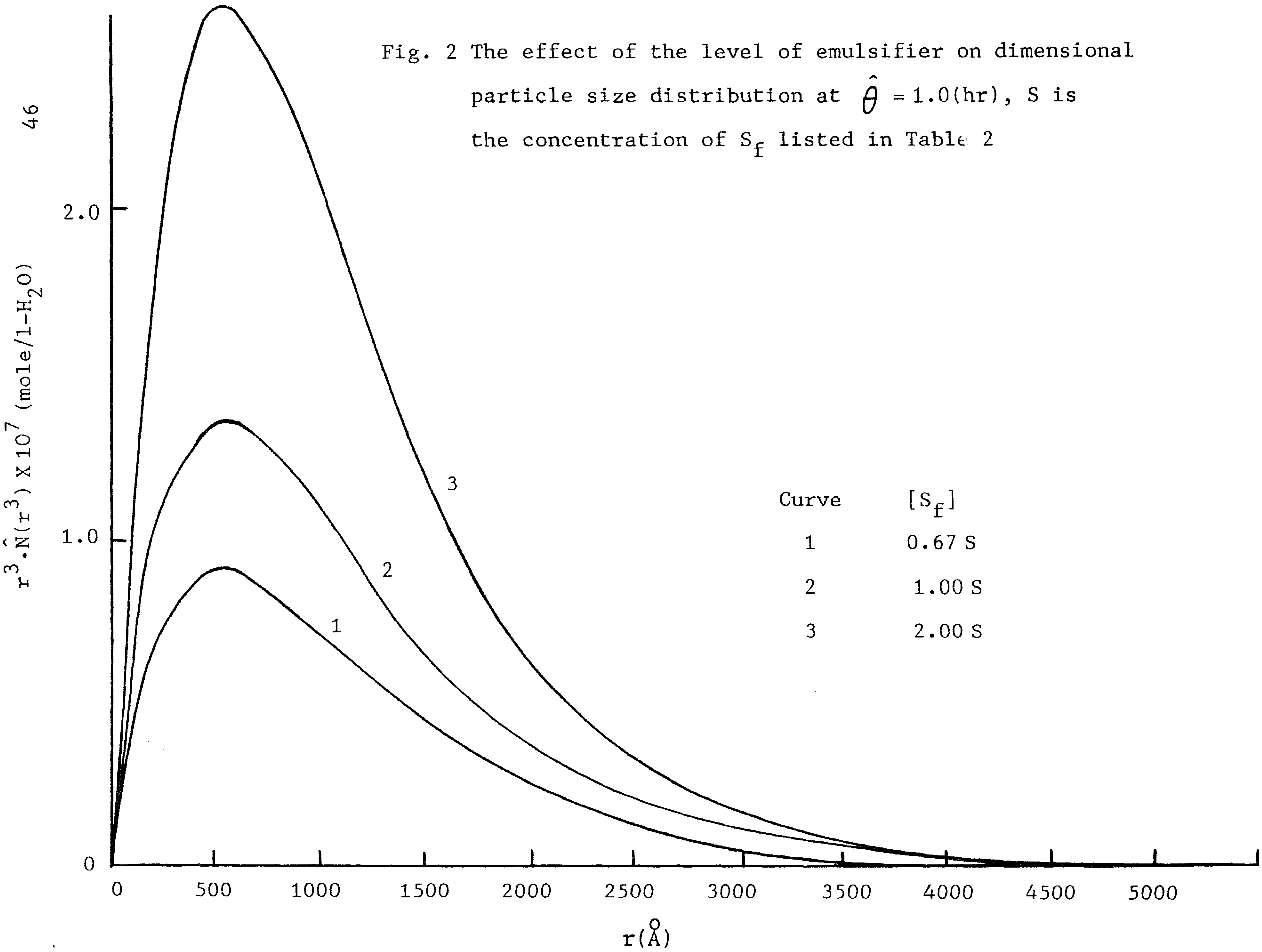


Fig. 2 The effect of the level of emulsifier on dimensional particle size distribution at $\hat{\theta}$ = 1.0(hr), S is the concentration of S_f listed in Table 2

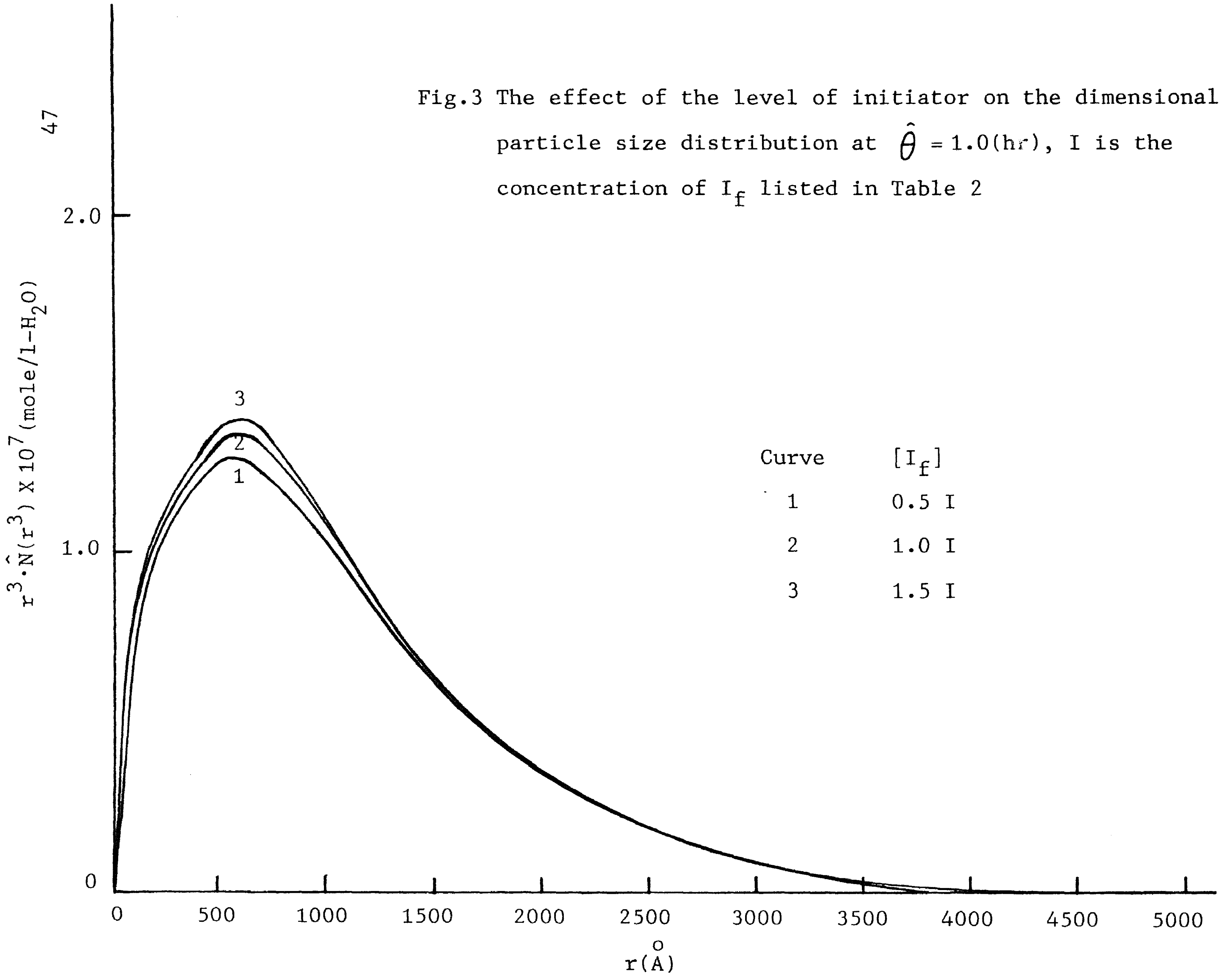


Fig.3 The effect of the level of initiator on the dimensional particle size distribution at $\hat{\theta} = 1.0$(hr), I is the concentration of I_f listed in Table 2

Fig.4 The effect of η on the total concentration of polymer particles vs. mean residence time; Solid line: $\eta = 0.4$; Dotted line: $\eta = 1.0$; o : Experimental data by Nomura$^{(11)}$

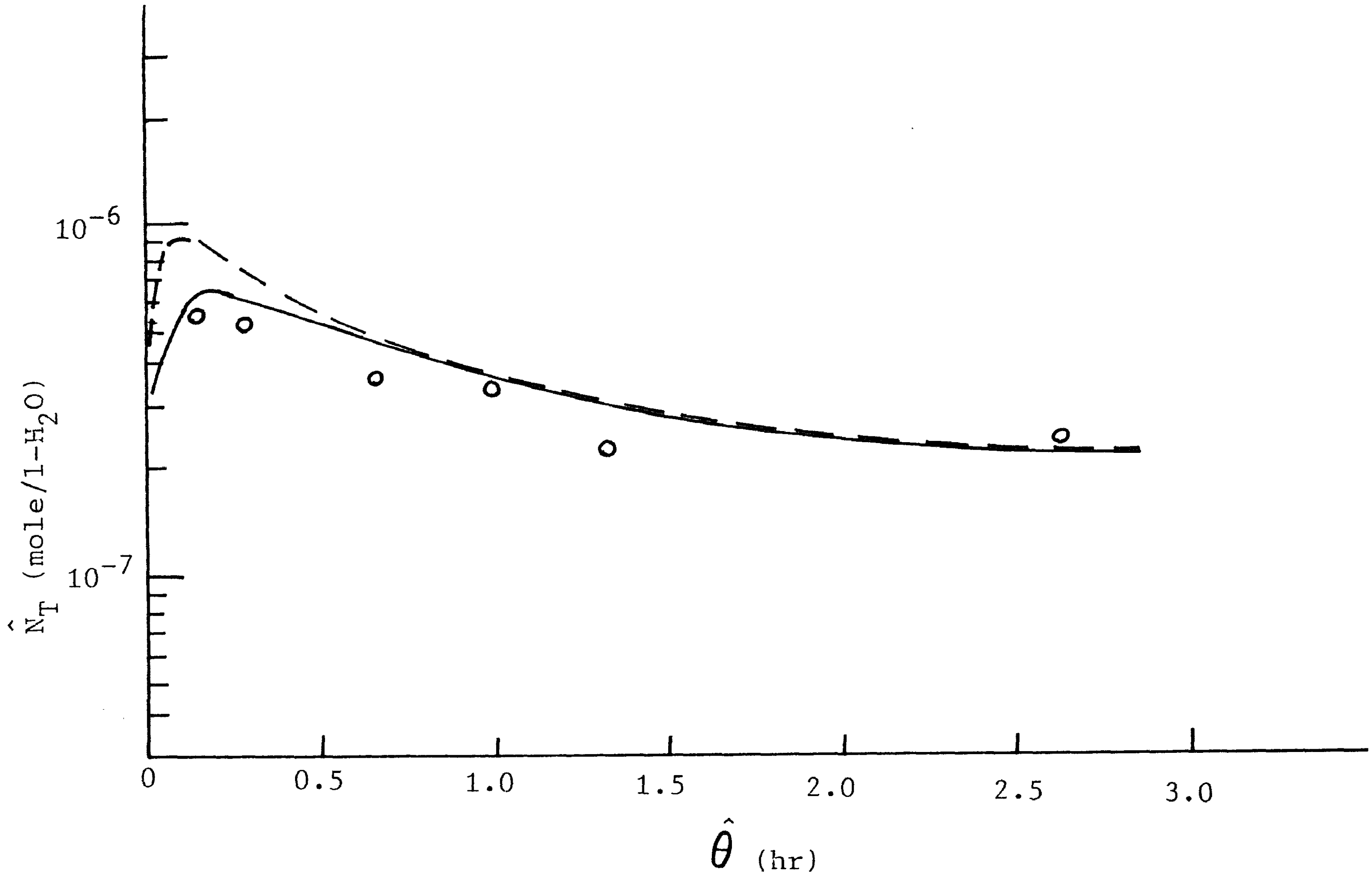


Fig.5 The effect of the level of emulsifier on the total concentration of polymer particles vs. mean residence time at $\eta = 0.4$; S is the concentration of S_f listed in Table 2

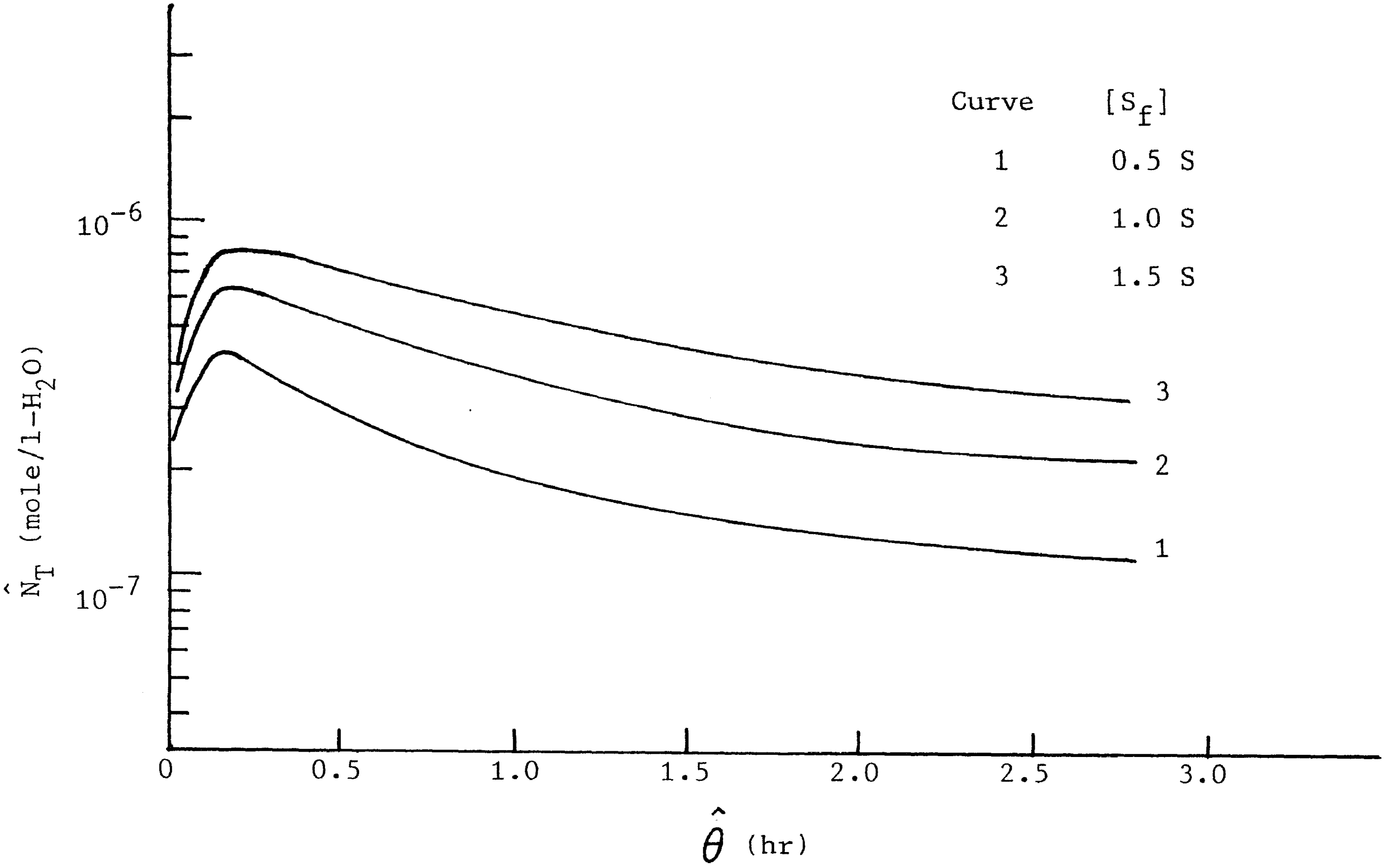


Fig.6 The effect of the level of initiator on the total concentration of polymer particles vs. mean residence time at $\eta = 0.4$; I is the concentration of I_f listed in Table 2

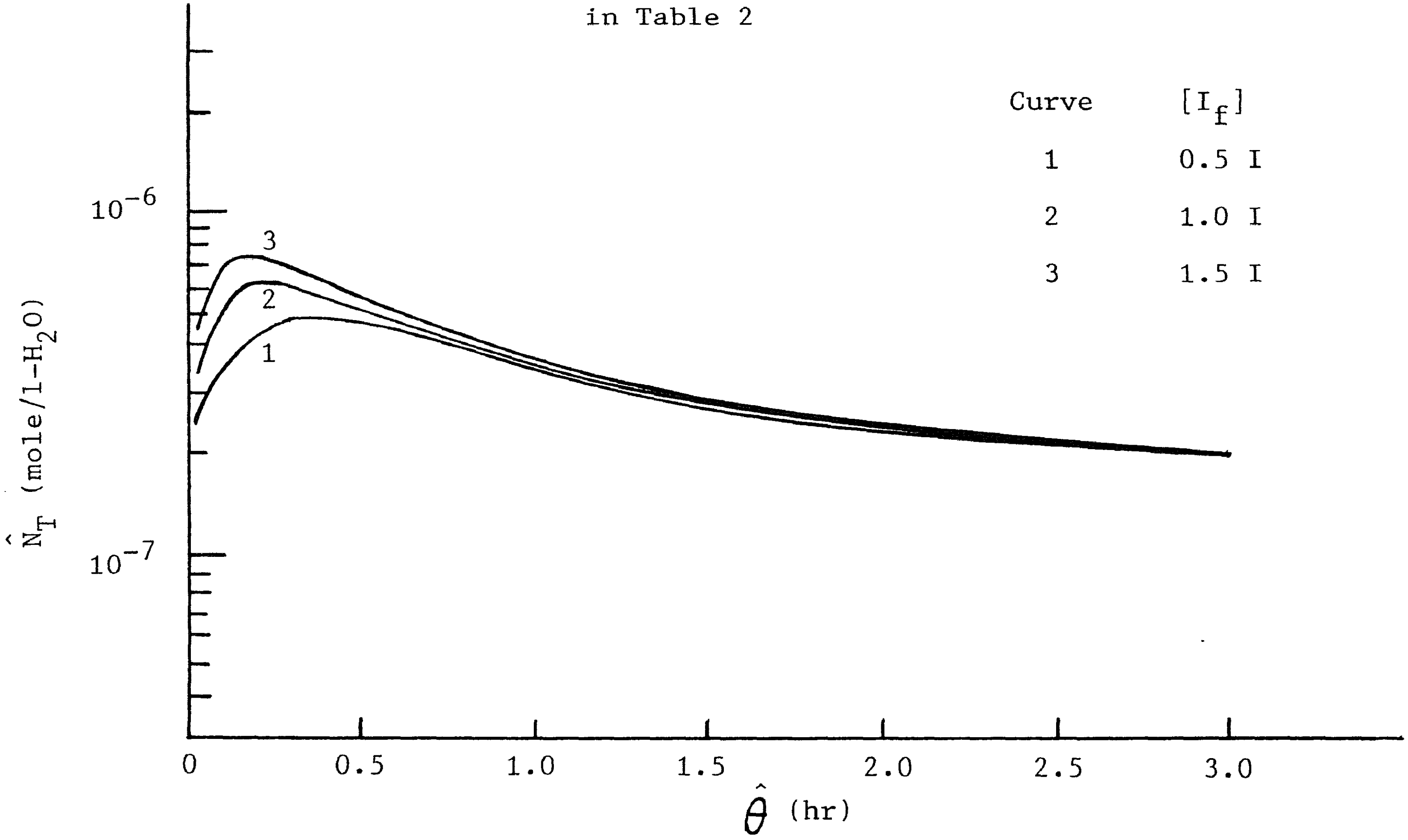


Fig. 7 System average number of radicals per polymer particle vs. mean residence time

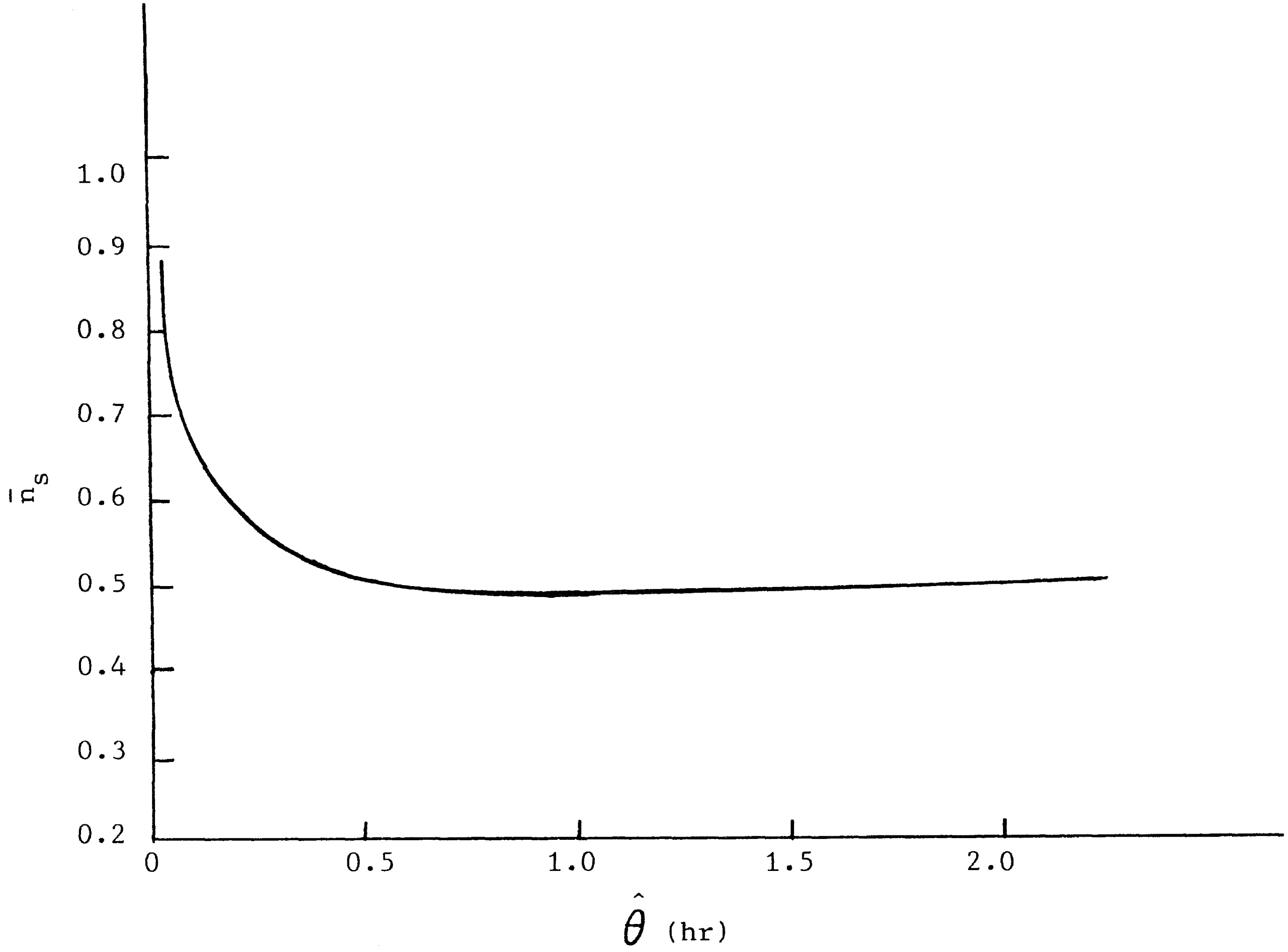


Fig.8 The effect of the level of emulsifier on the system average number of radicals per polymer particle at $\hat{\theta} = 1.0$(hr); S is the concentration of S_f listed in Table 2

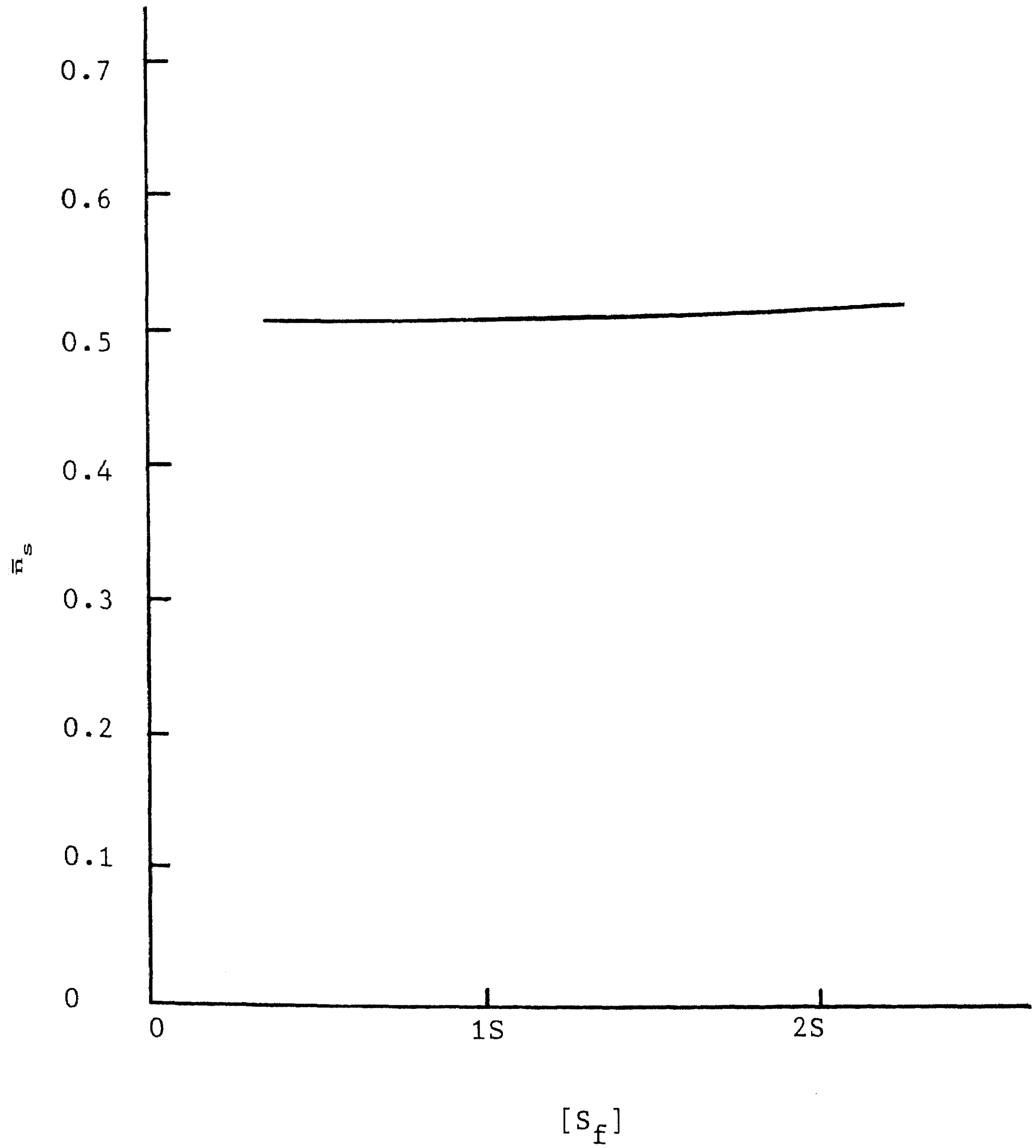


Fig. 9 The effect of the level of initiator on the system average number of radicals per polymer particle at $\hat{\theta}$ = 1.0(hr); I is the concentration of I_f listed in Table 2

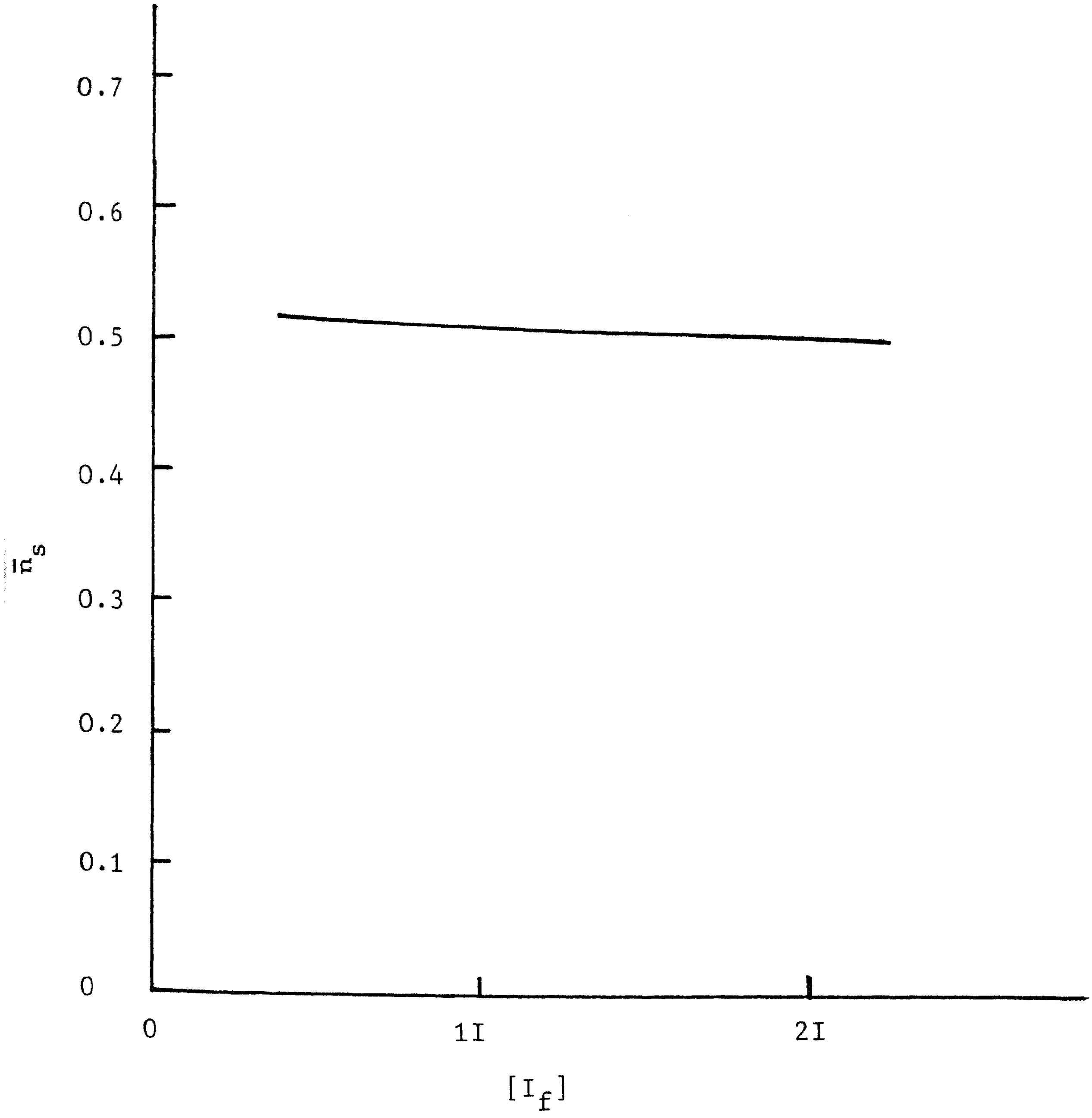


Fig.10 Conversion vs. mean residence time; Solid line: η =0.4; Dotted line: η = 1.0; o: Experimental data by Nomura(11)

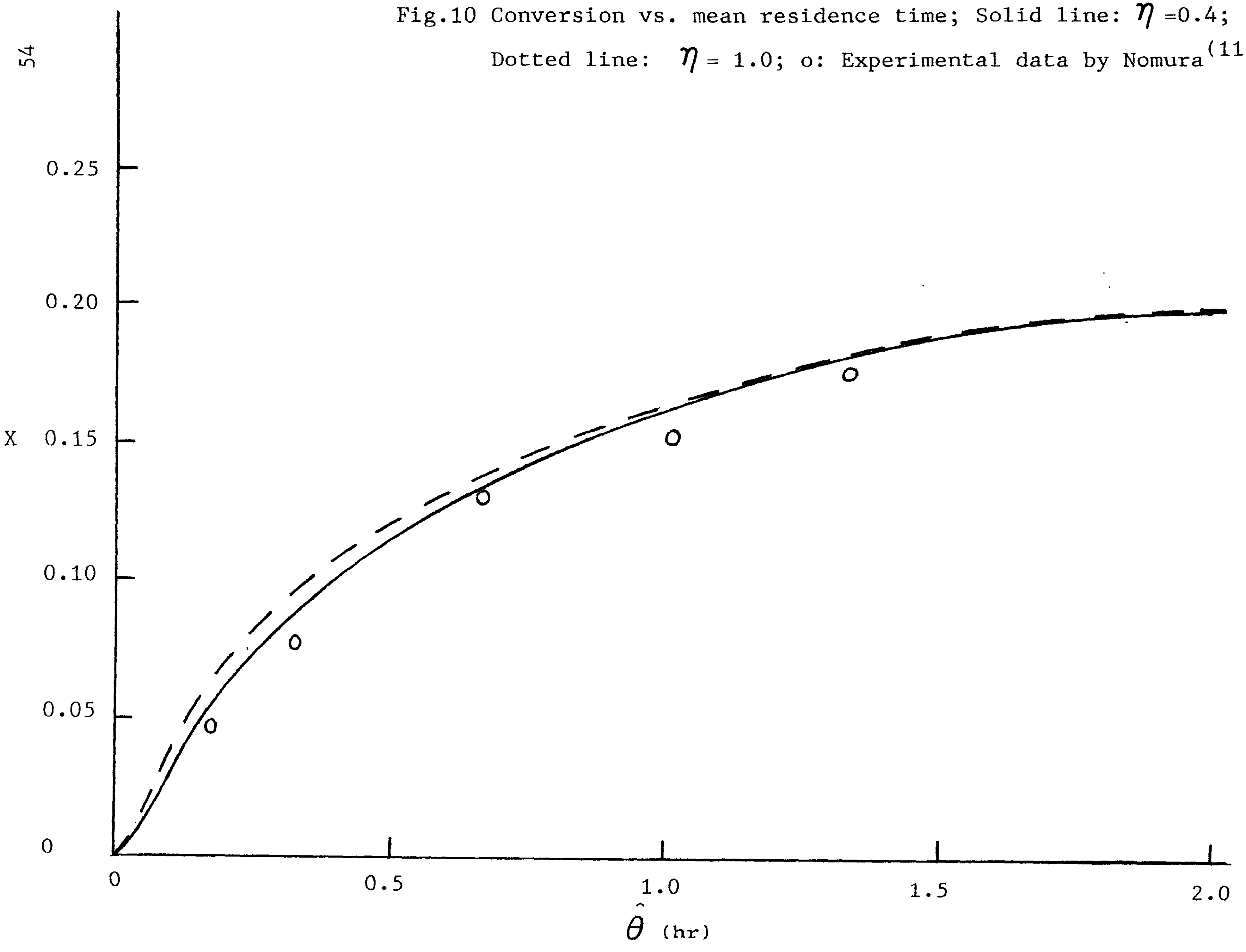


Fig.11 The effect of the level of emulsifier on the conversion under different mean residence times; S is the concentration of S_f listed in Table 2

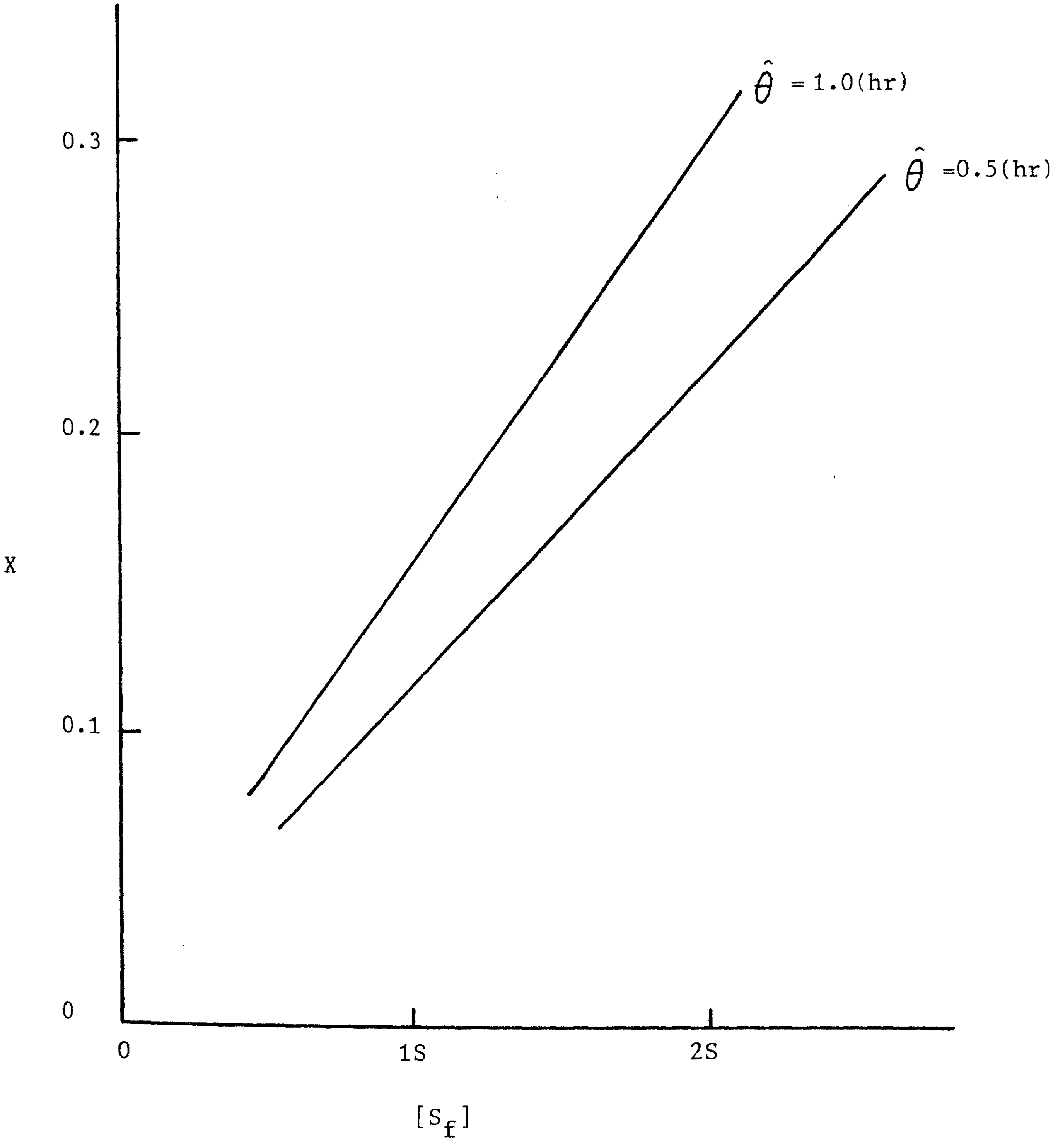


Fig.12 The effect of the level of initiator on the conversion under different mean residence times; I is the concentration of I_f listed in Table 2

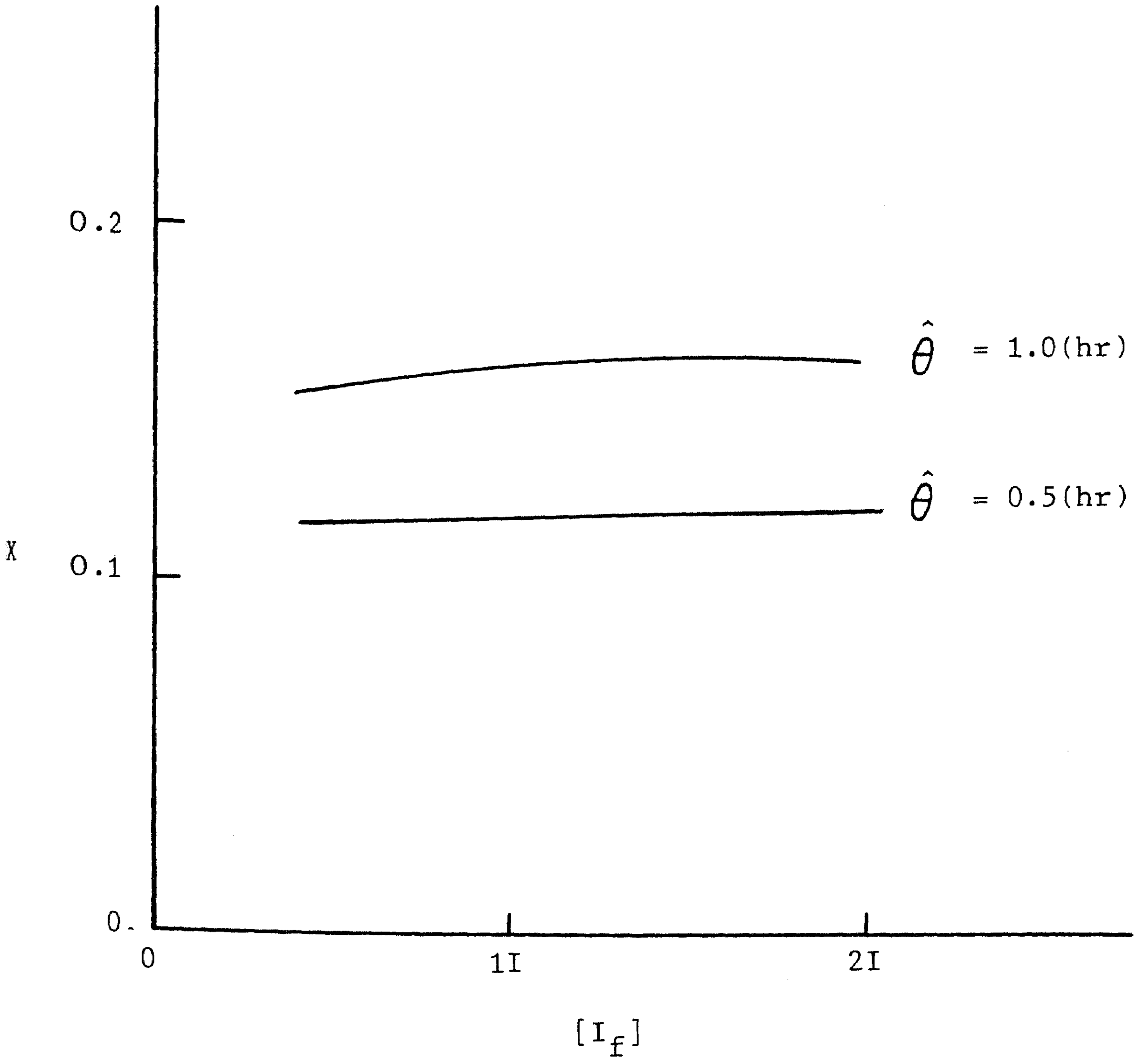


Fig.13 Number average radius and weight average radius of polymer particle vs. mean residence time

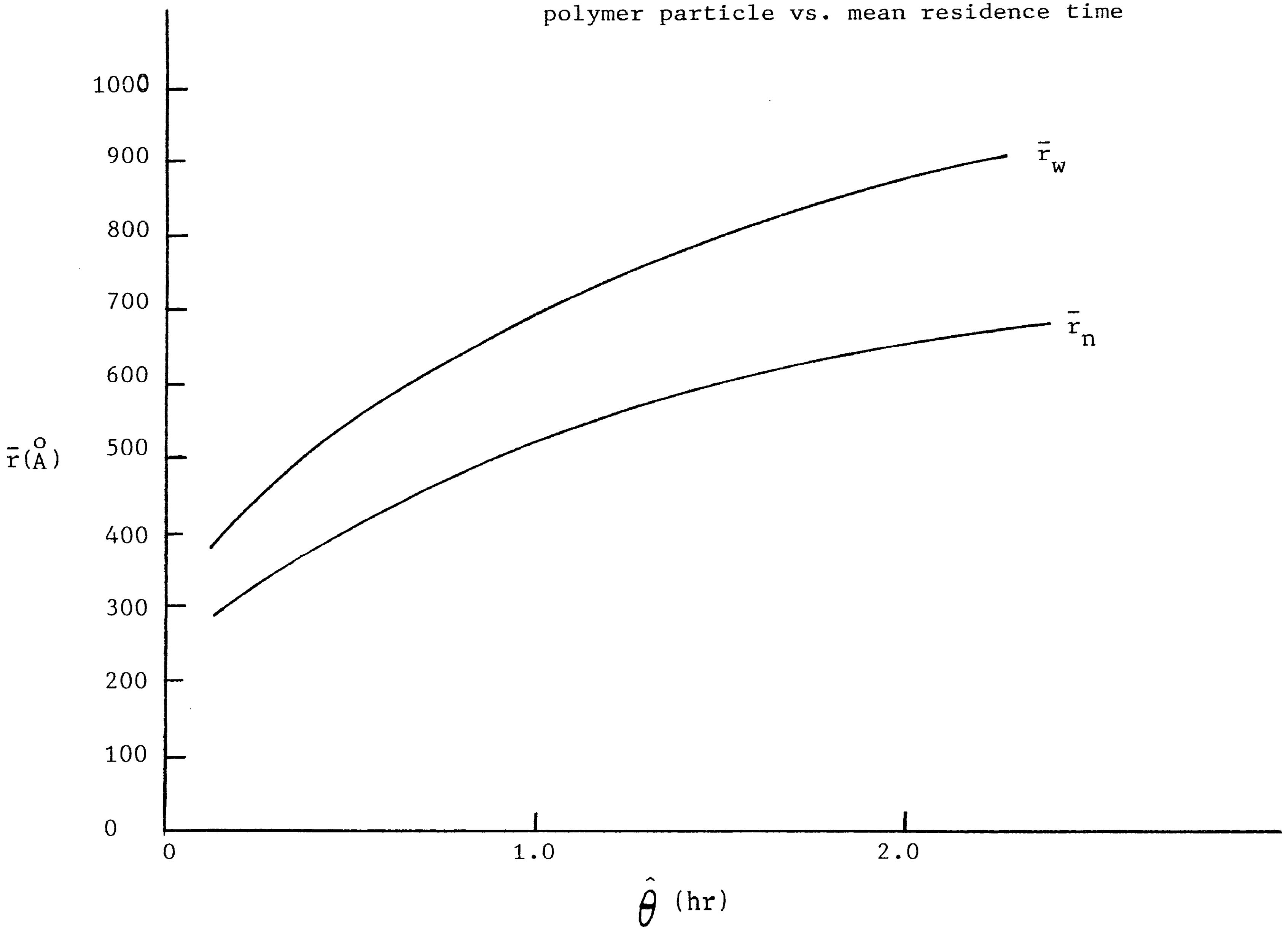
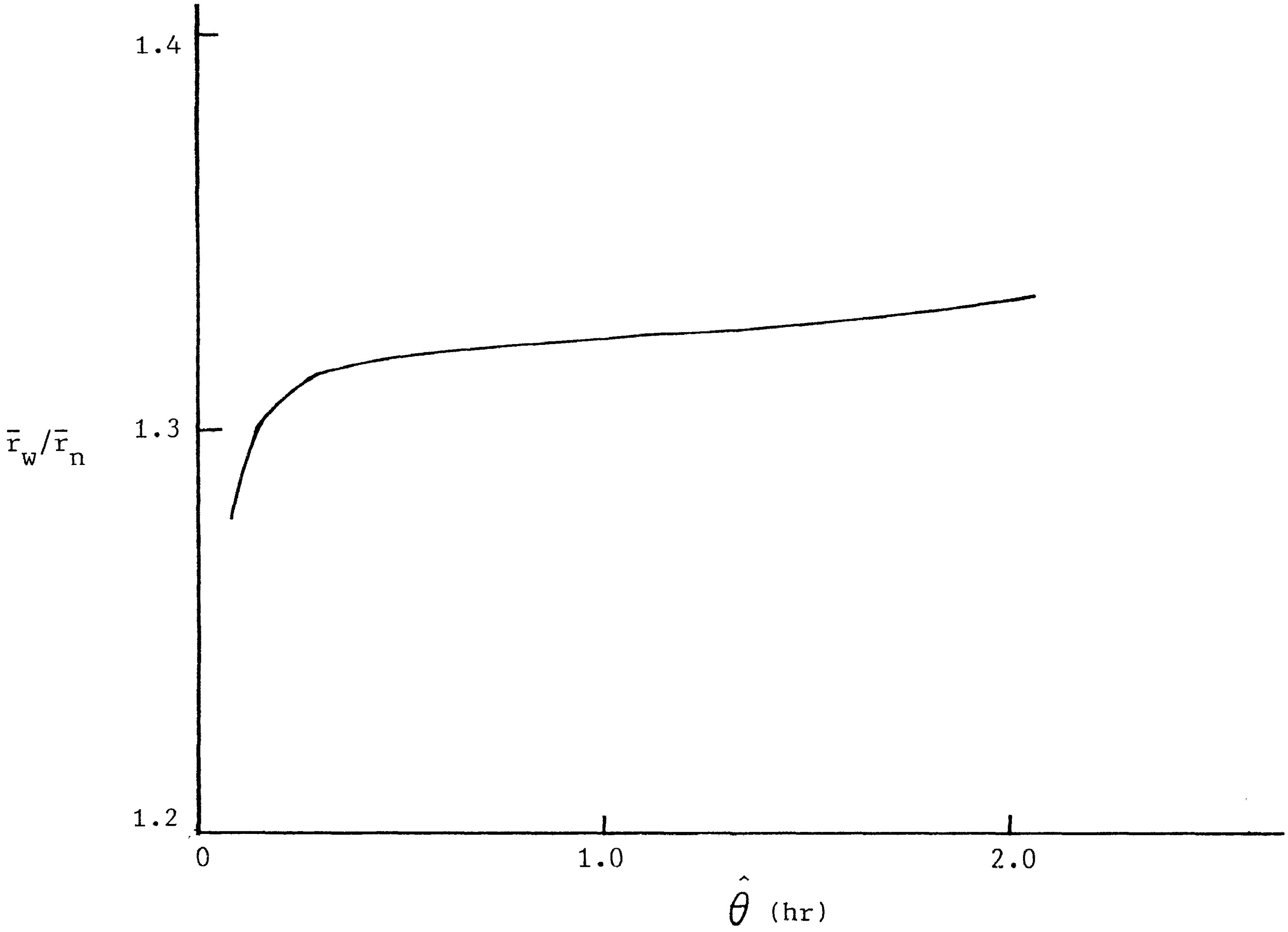


Fig.14 Polydispersity of radius vs. mean residence time



APPENDIX C

THE FIGURES OF CONTINUOUS EMULSION POLYMERIZATION OF VINYL ACETATE

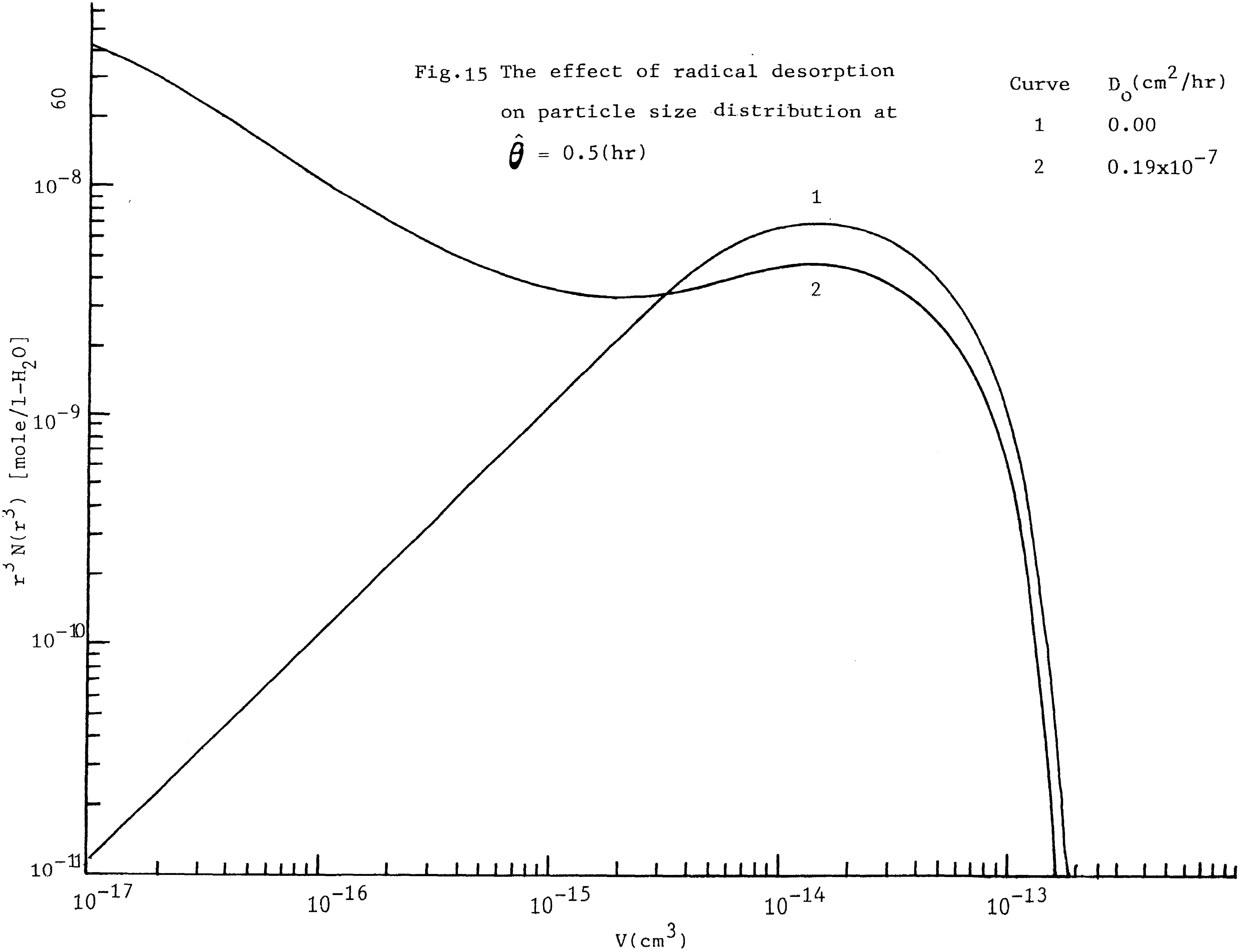


Fig.15 The effect of radical desorption on particle size distribution at $\hat{\theta}$ = 0.5(hr)

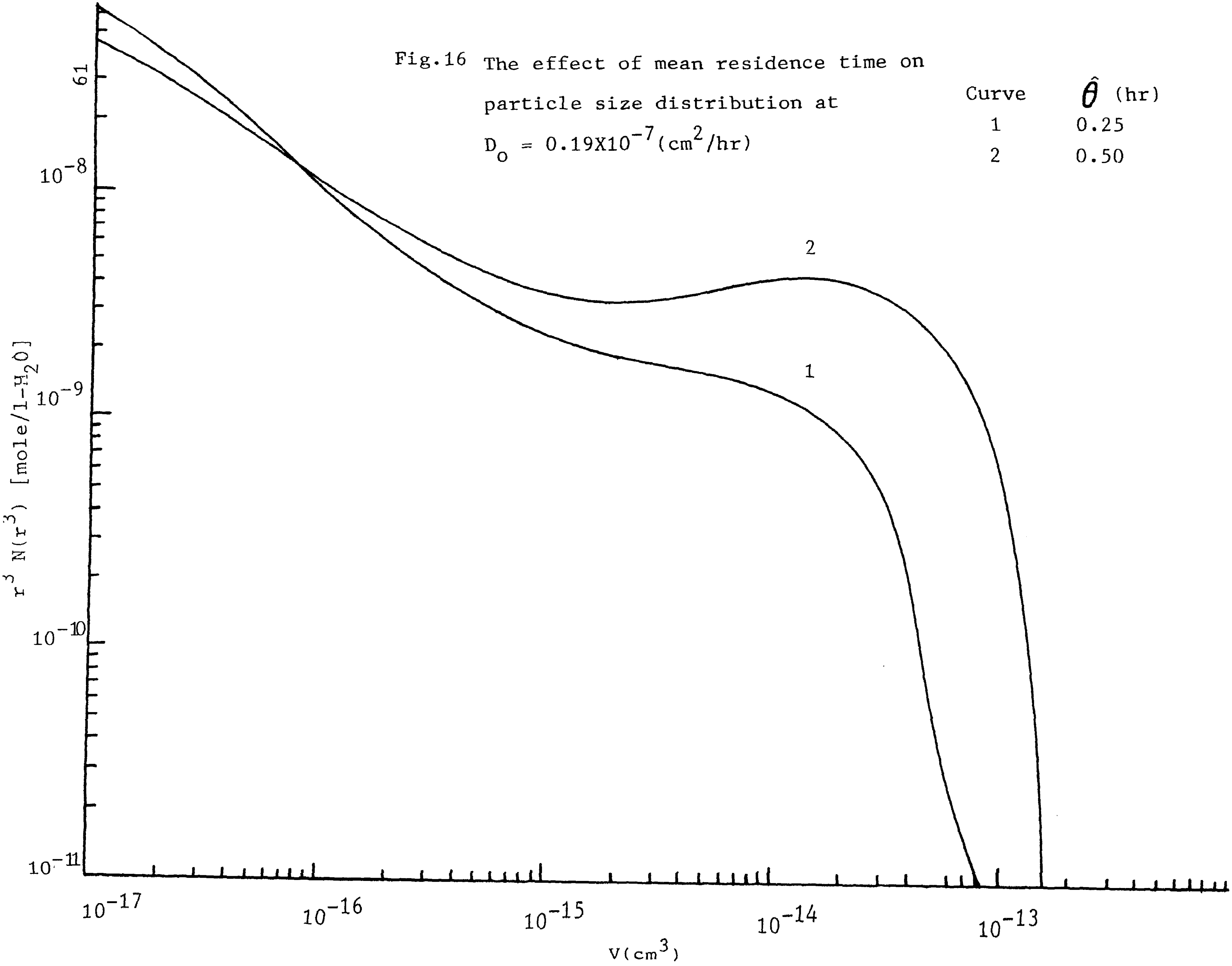


Fig.16 The effect of mean residence time on particle size distribution at $D_o = 0.19 \times 10^{-7} (cm^2/hr)$

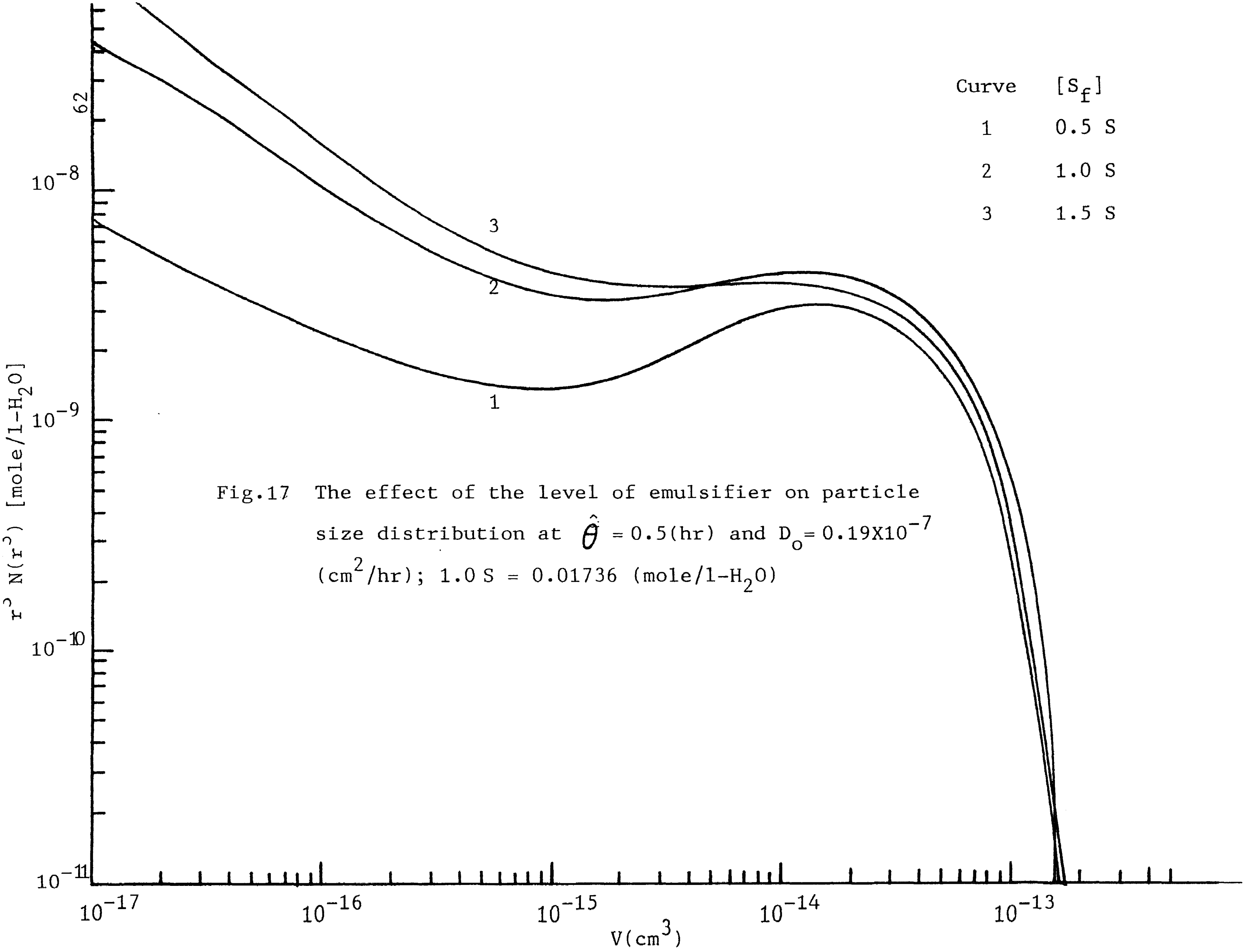


Fig.17 The effect of the level of emulsifier on particle size distribution at $\hat{\theta} = 0.5$(hr) and $D_o = 0.19 \times 10^{-7}$ (cm^2/hr); 1.0 S = 0.01736 (mole/l-H_2O)

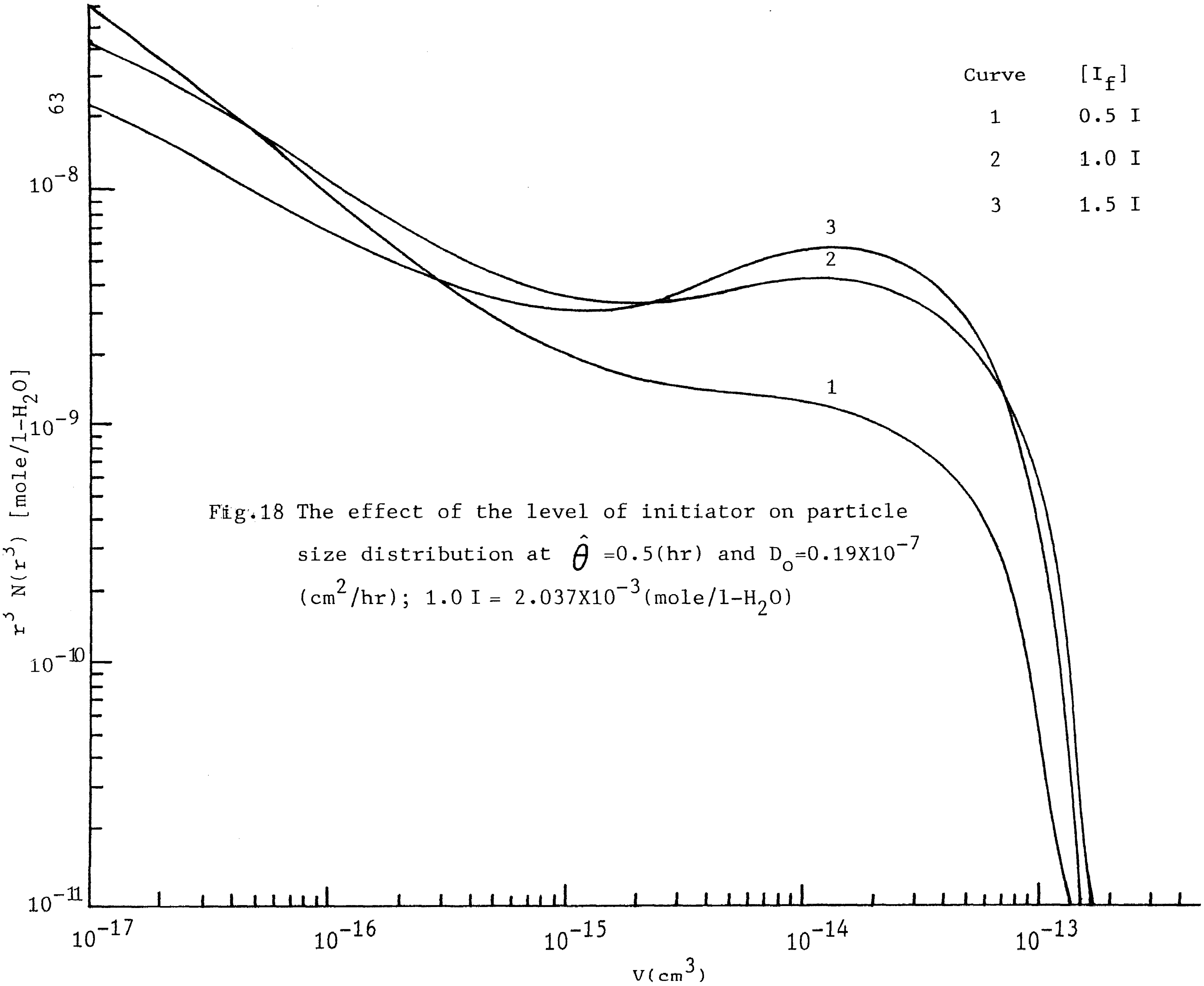


Fig.18 The effect of the level of initiator on particle size distribution at $\hat{\theta}$ =0.5(hr) and D_o=0.19X10^{-7} (cm^2/hr); 1.0 I = 2.037X10^{-3}(mole/l-H_2O)

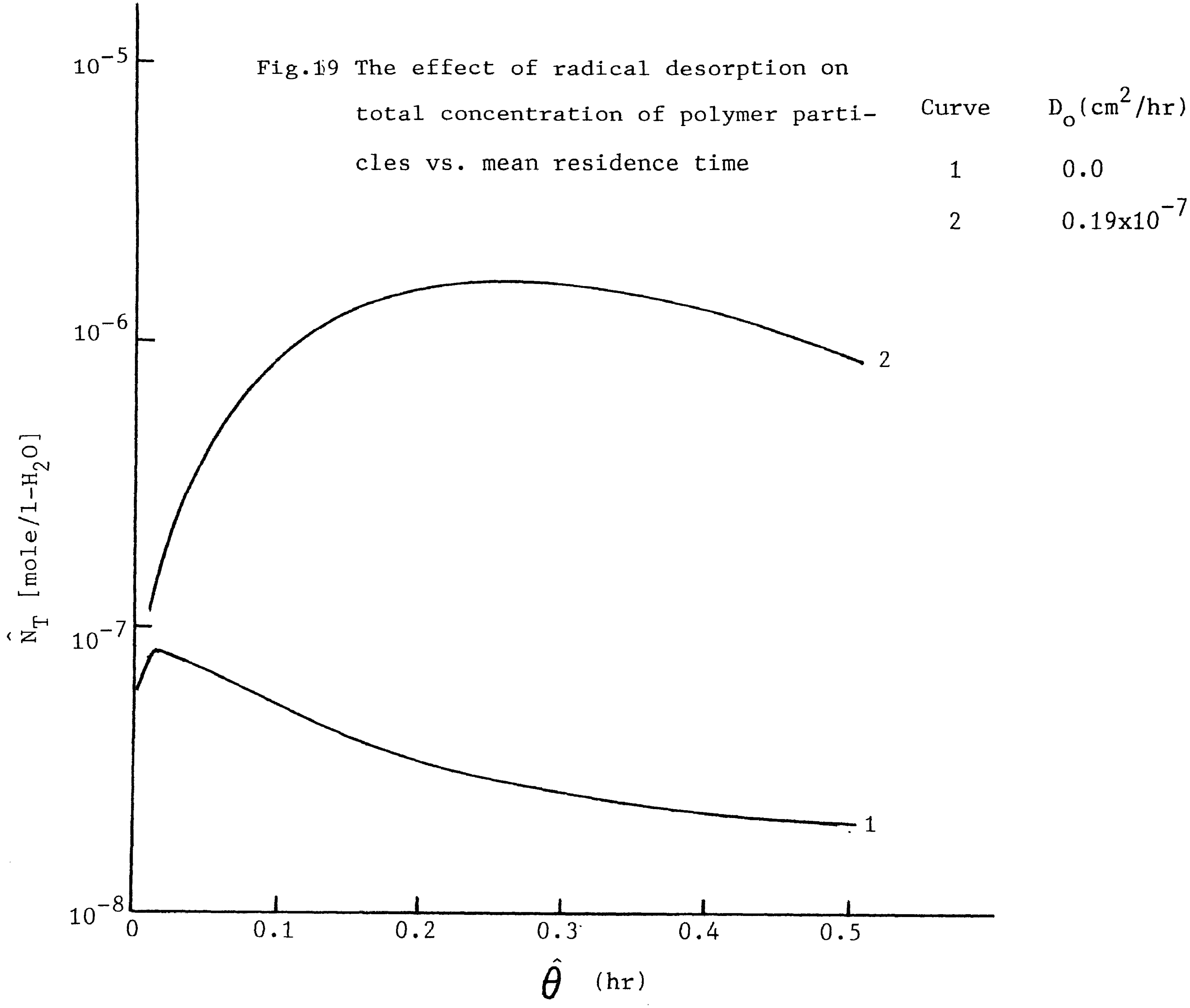


Fig.19 The effect of radical desorption on total concentration of polymer particles vs. mean residence time

Fig.20 The effect of the level of emulsifier on total concentration of polymer particles vs. mean residence time at D_o=0.19X10^{-7} (cm^2/hr); 1.0 S = 0.01736(mole/l-H_2O)

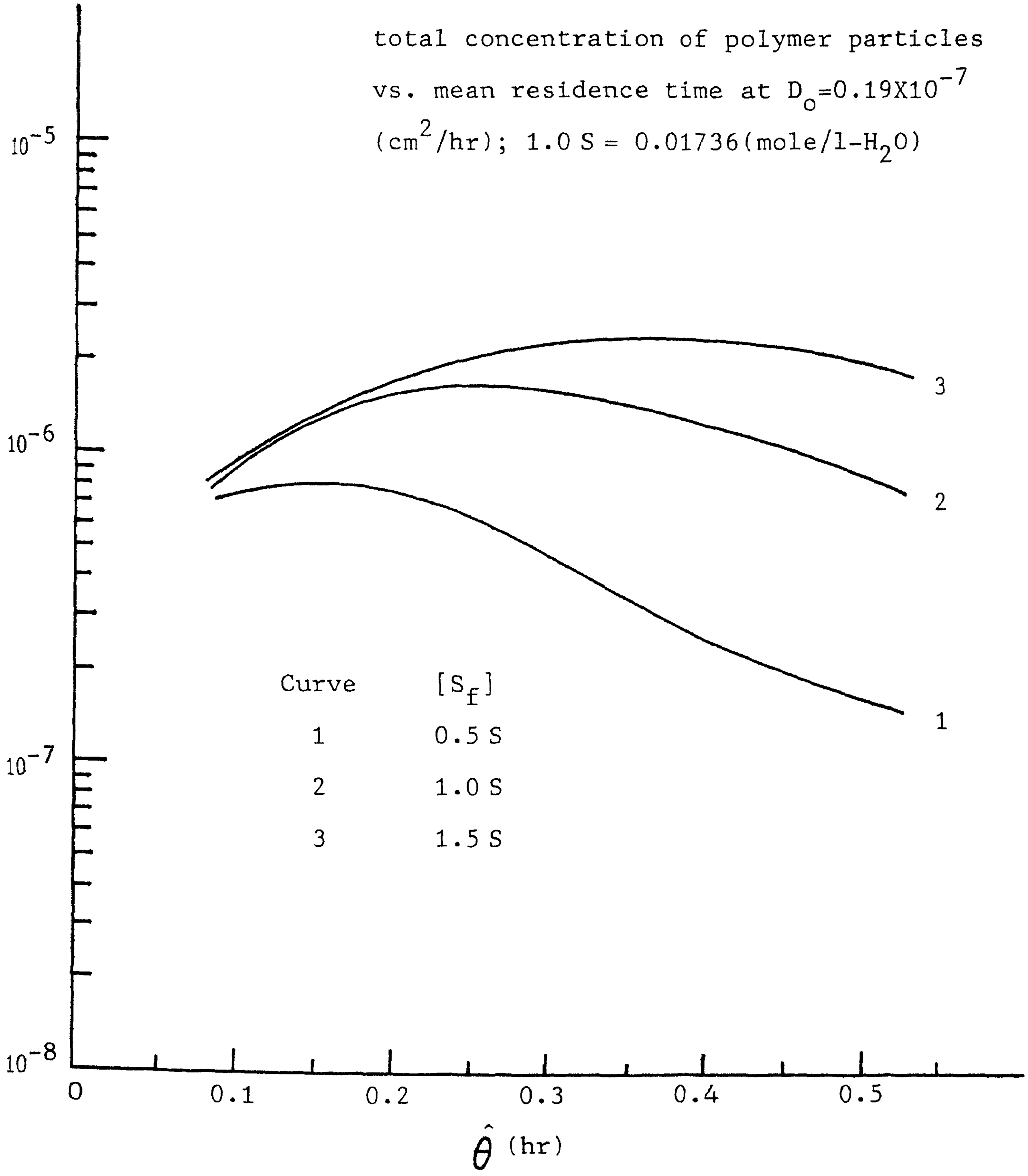
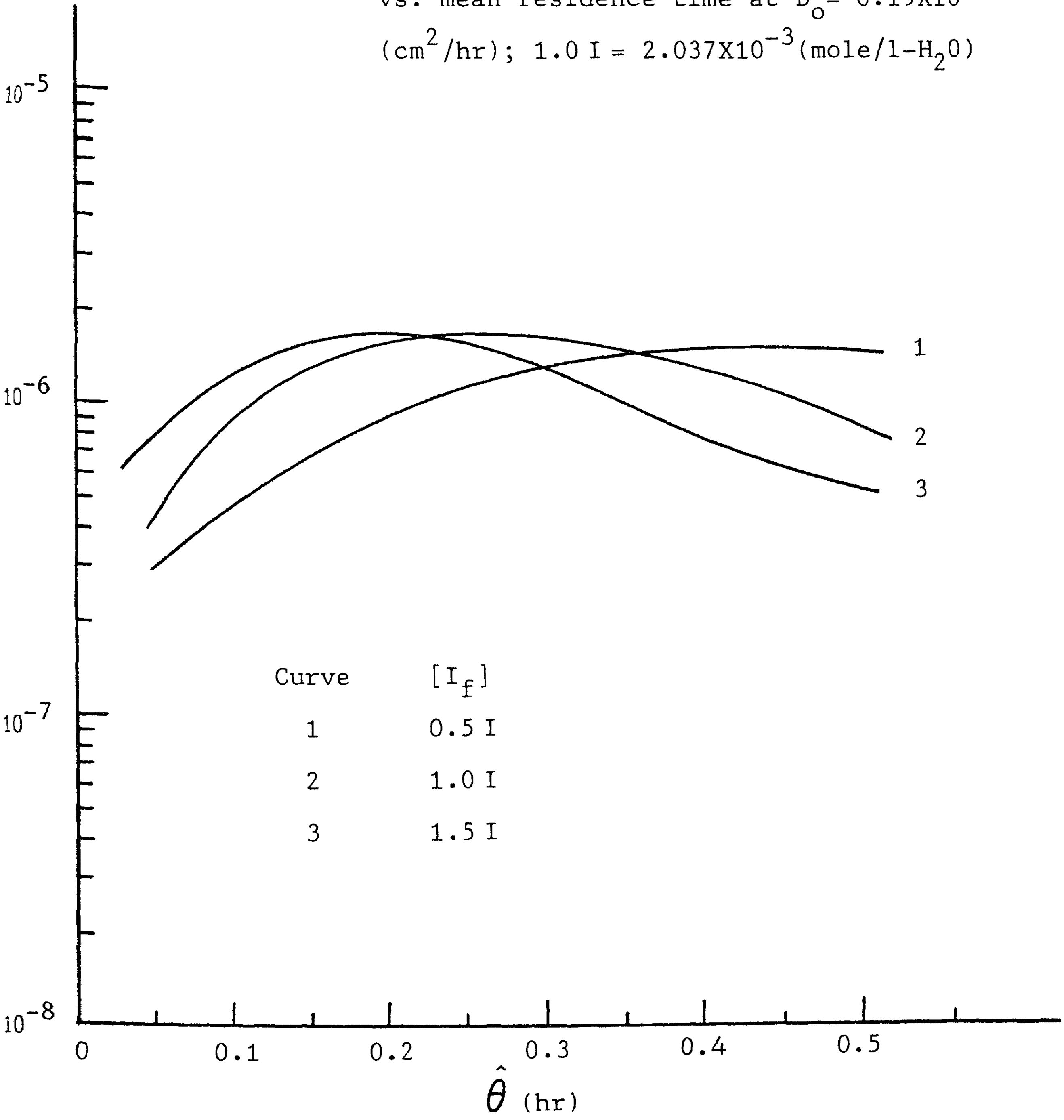


Fig.21 The effect of the level of initiator on total concentration of polymer particles vs. mean residence time at $D_o = 0.19 \times 10^{-7}$ (cm^2/hr); 1.0 I = 2.037×10^{-3} ($mole/l-H_2O$)



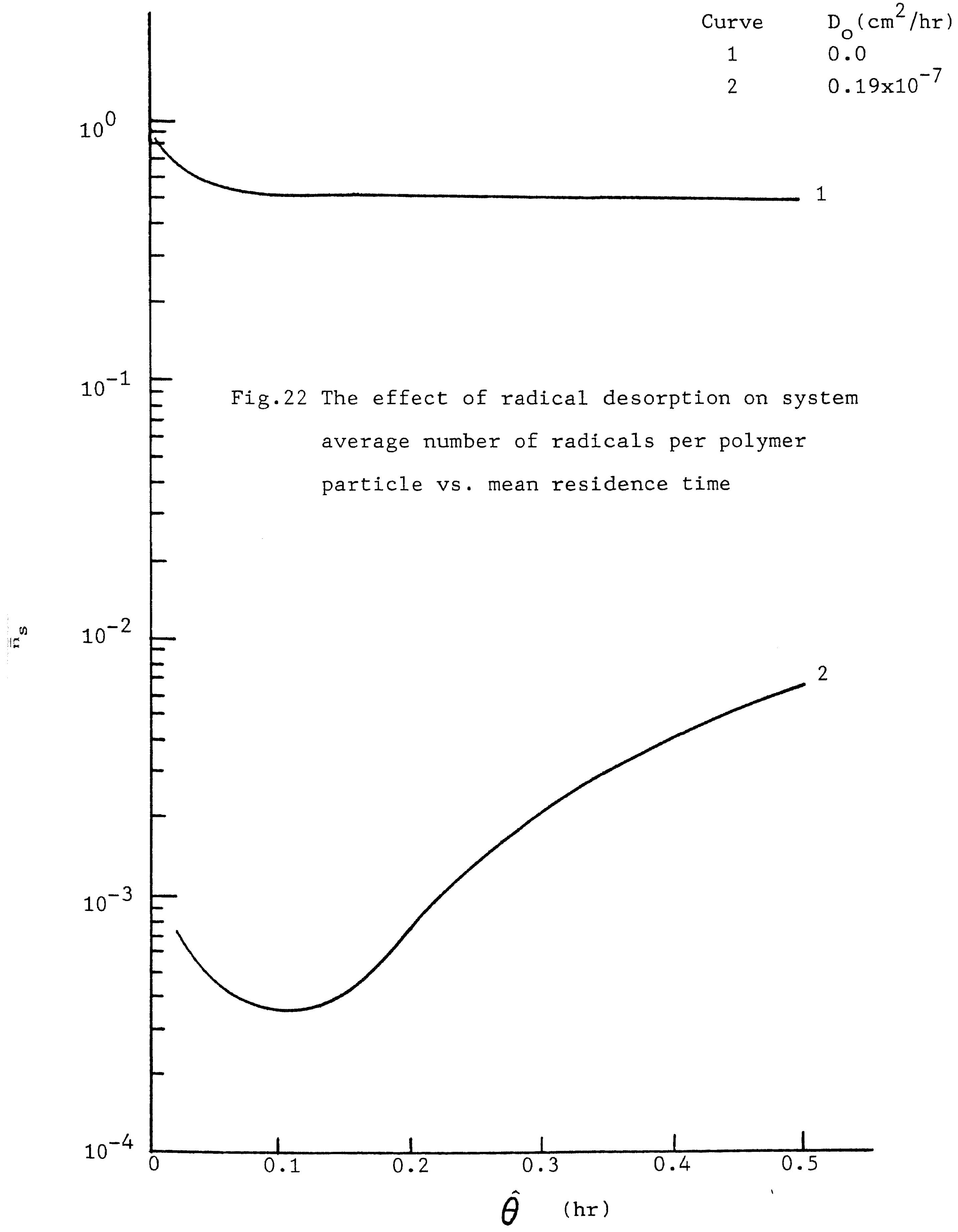


Fig.22 The effect of radical desorption on system average number of radicals per polymer particle vs. mean residence time

Fig.23 The effect of the level of emulsifier on system average number of radicals per polymer particle under different mean residence times at $D_o = 0.19 \times 10^{-7}$ (cm^2/hr); 1S = 0.01736(mole/l-H_2O)

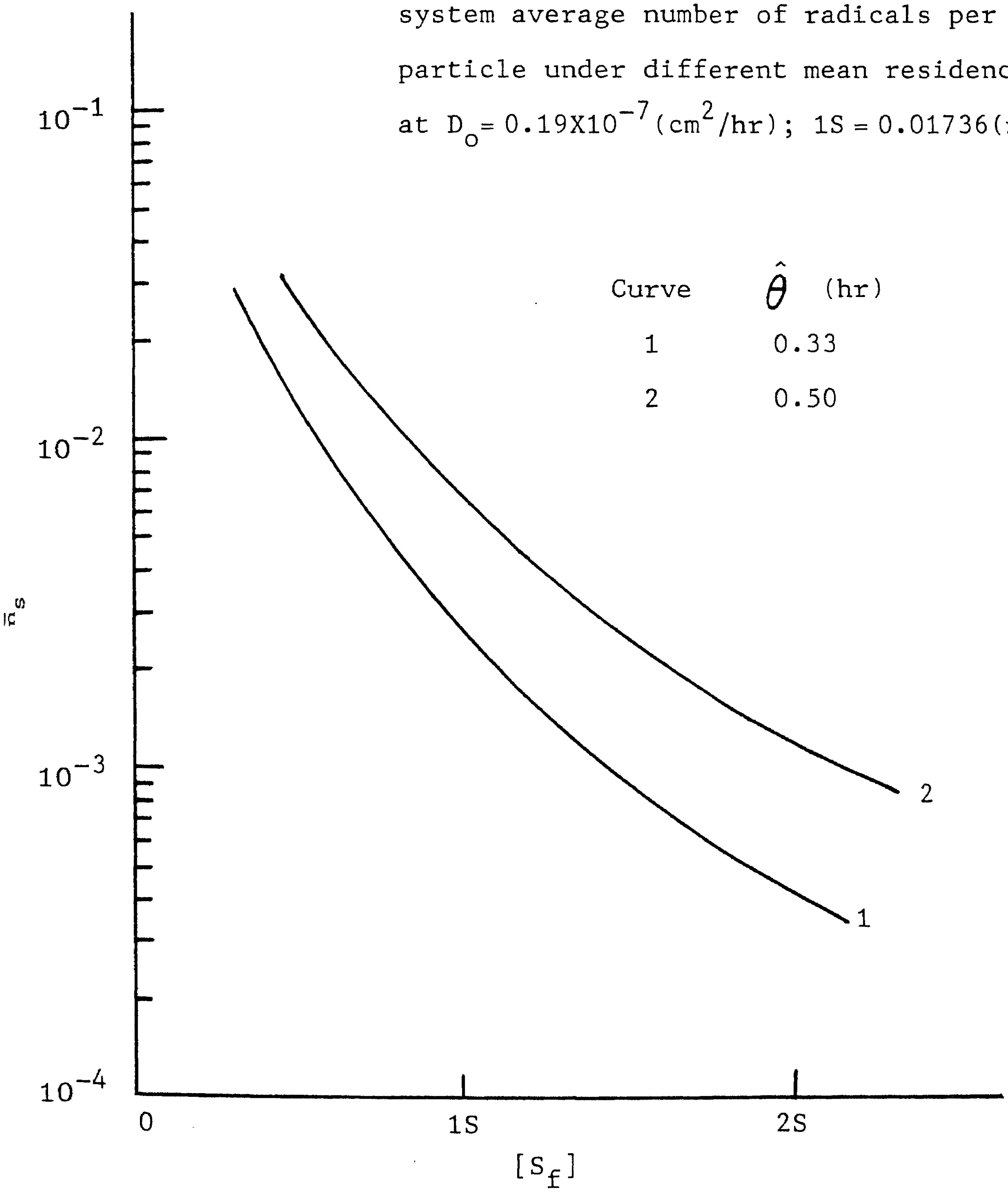
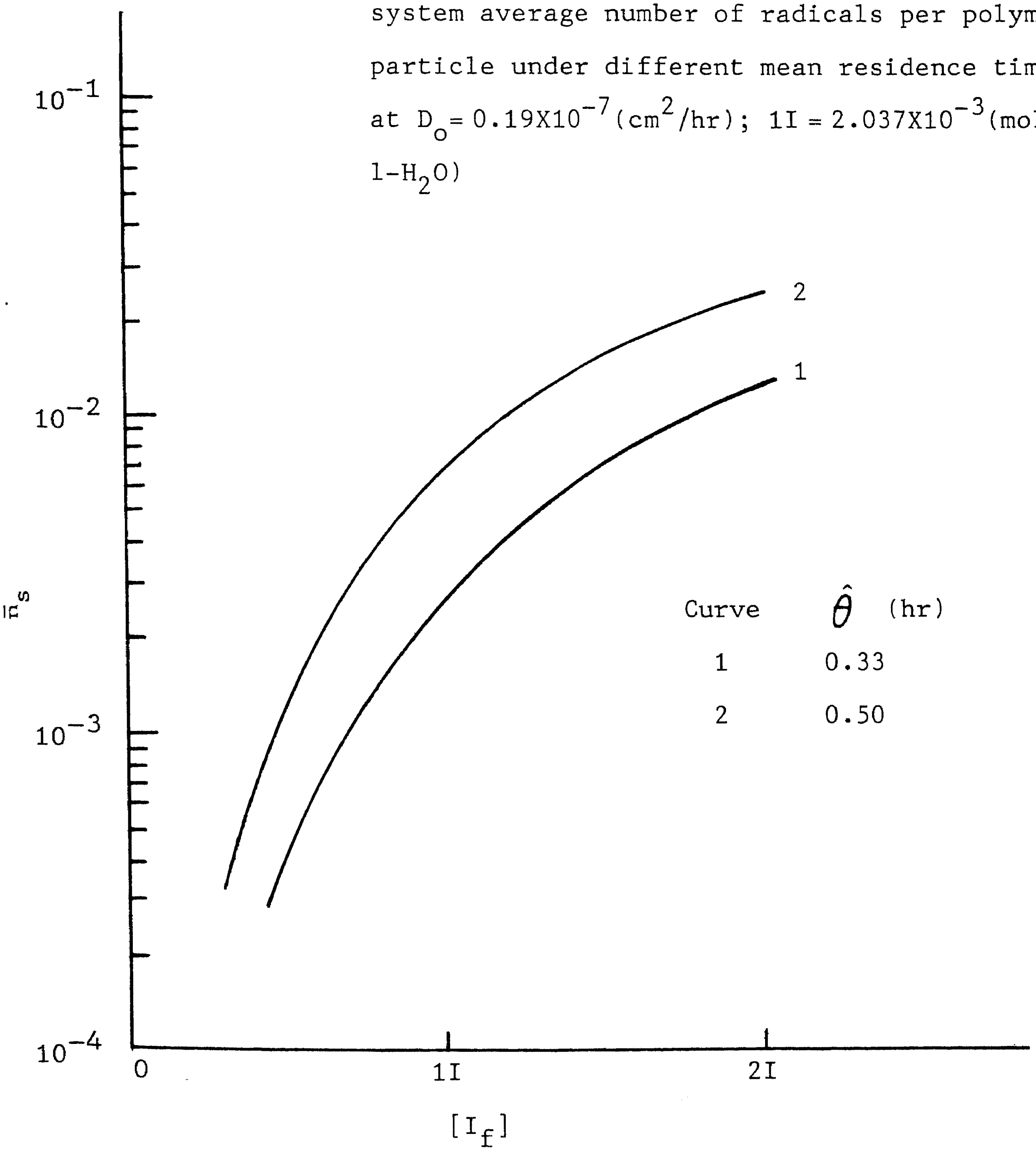


Fig.24 The effect of the level of initiator on system average number of radicals per polymer particle under different mean residence times at $D_o = 0.19 \times 10^{-7}$ (cm^2/hr); $1I = 2.037 \times 10^{-3}$ (mole/ l-H_2O)



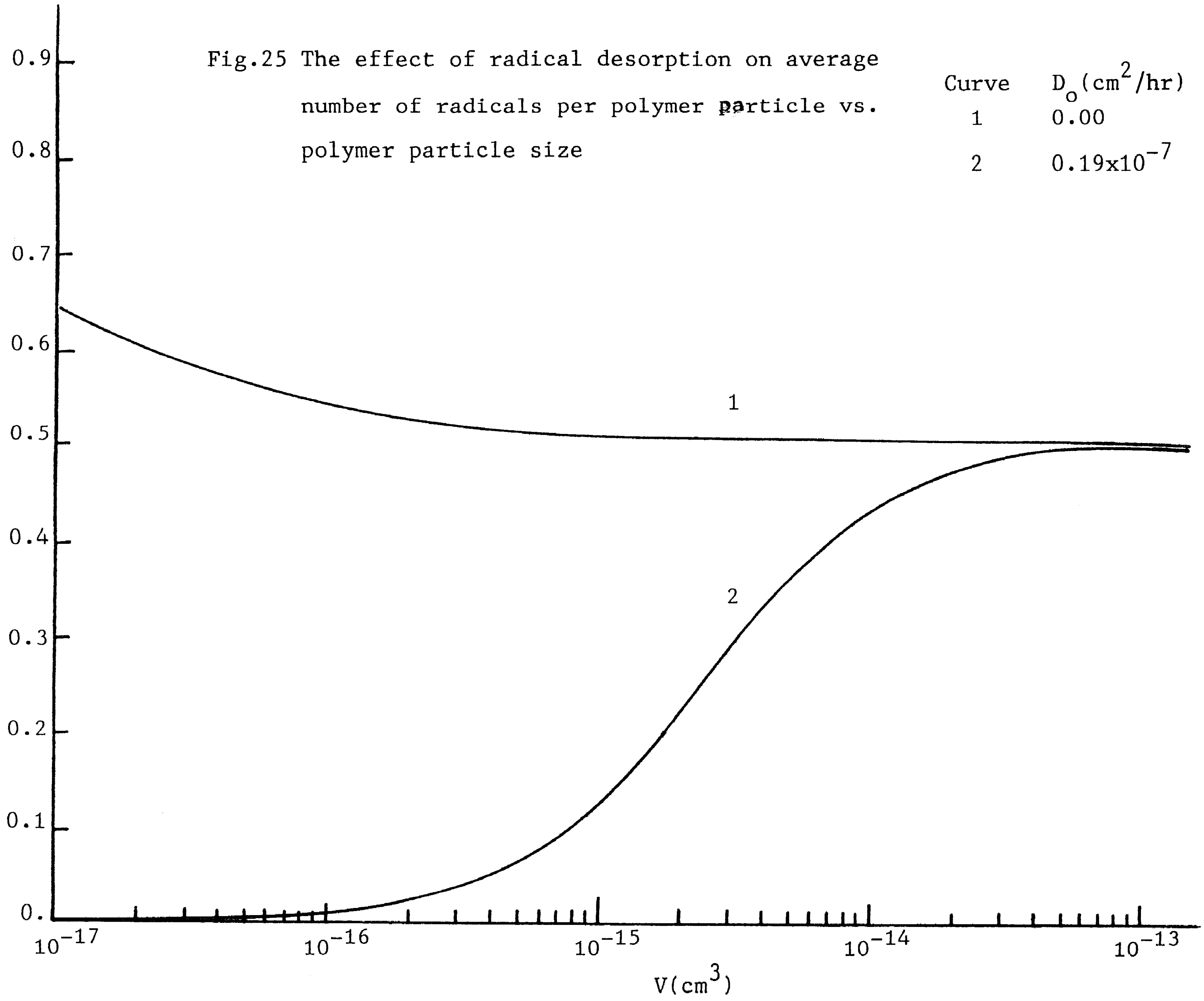
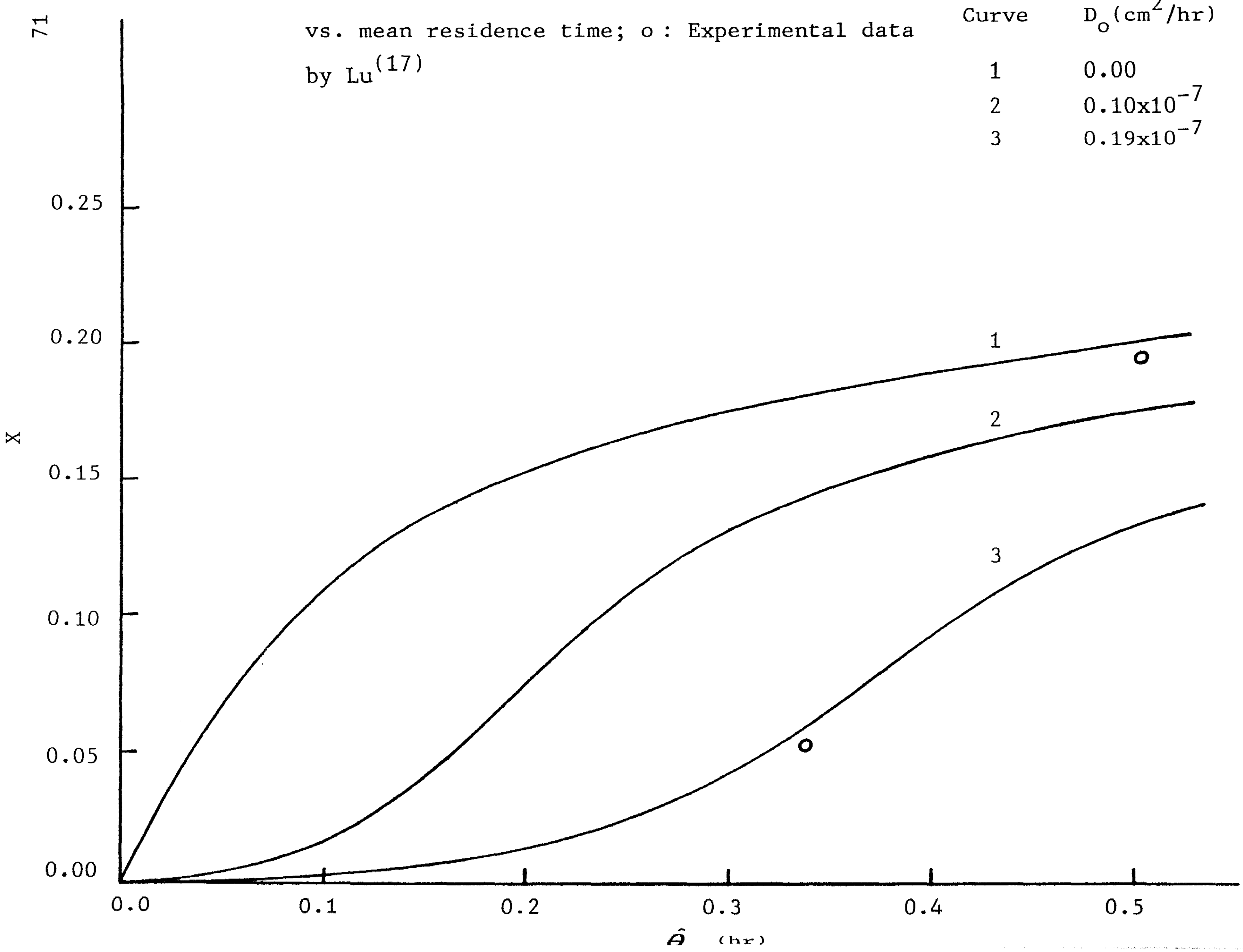


Fig.25 The effect of radical desorption on average number of radicals per polymer particle vs. polymer particle size

Fig.26 The effect of radical desorption on conversion vs. mean residence time; o : Experimental data by Lu(17)



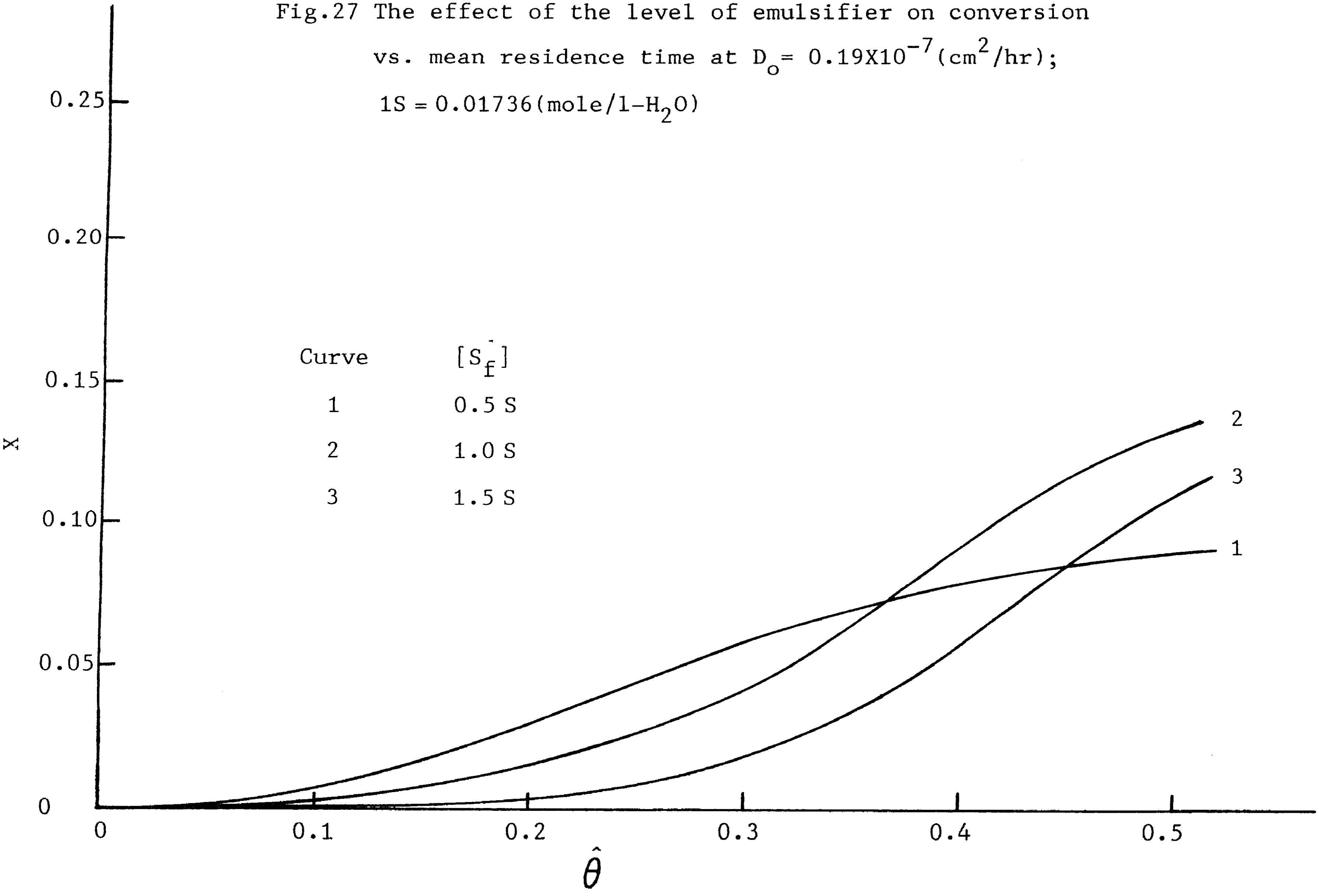
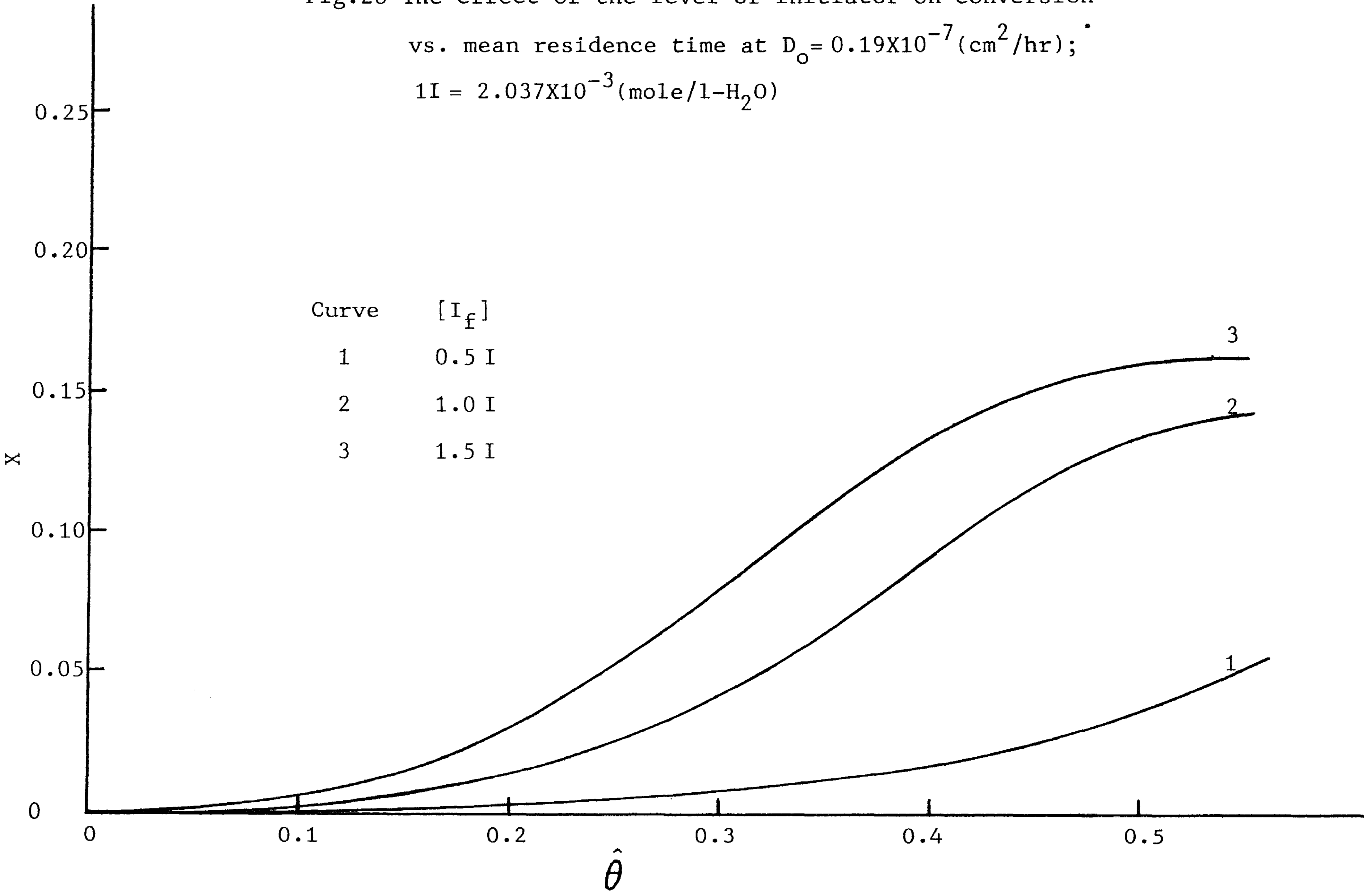


Fig.27 The effect of the level of emulsifier on conversion vs. mean residence time at $D_o = 0.19 \times 10^{-7} (cm^2/hr)$; $1S = 0.01736 (mole/l-H_2O)$

Fig.28 The effect of the level of initiator on conversion vs. mean residence time at $D_o = 0.19 X 10^{-7} (cm^2/hr)$; $1I = 2.037 X 10^{-3} (mole/l-H_2O)$



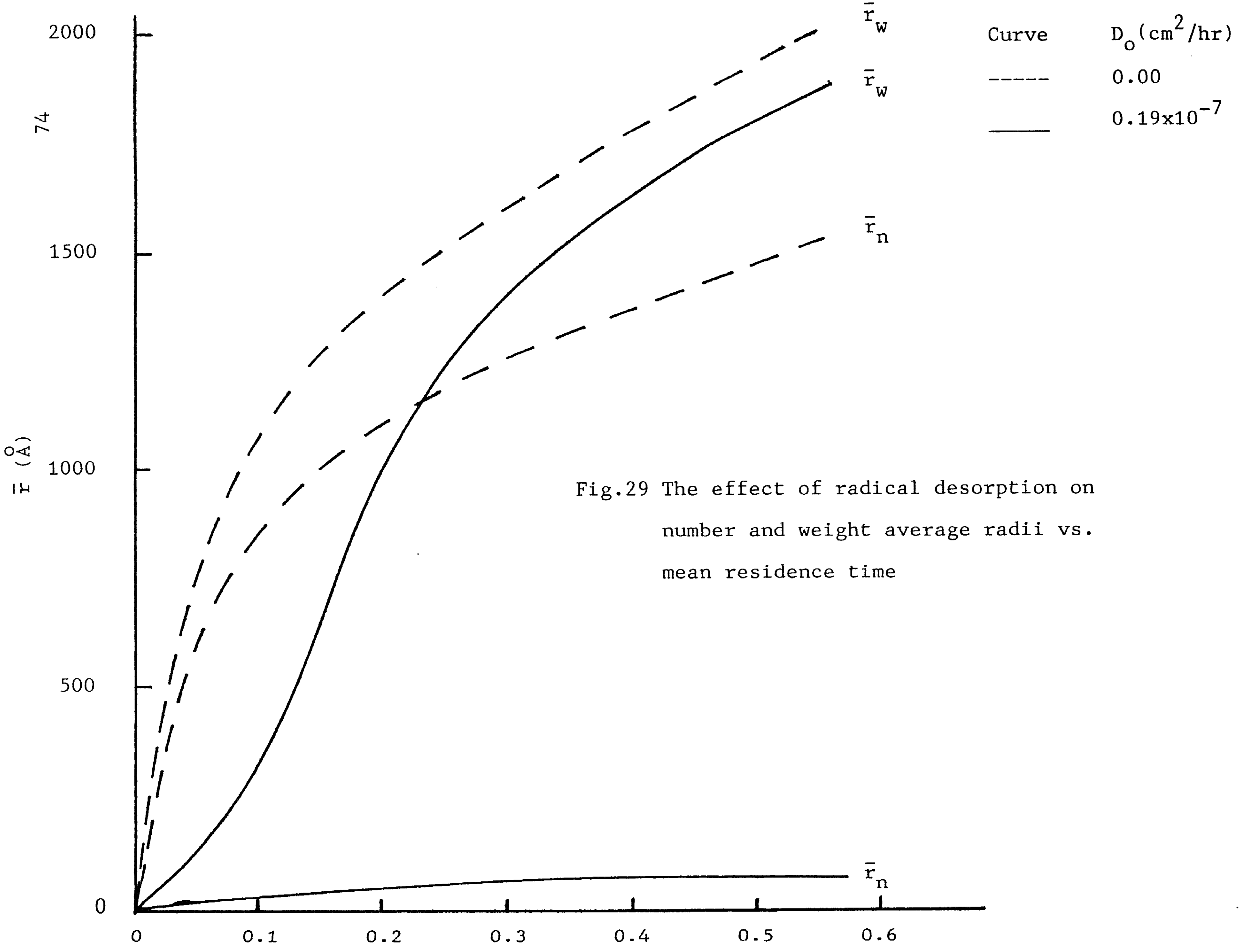


Fig.29 The effect of radical desorption on number and weight average radii vs. mean residence time

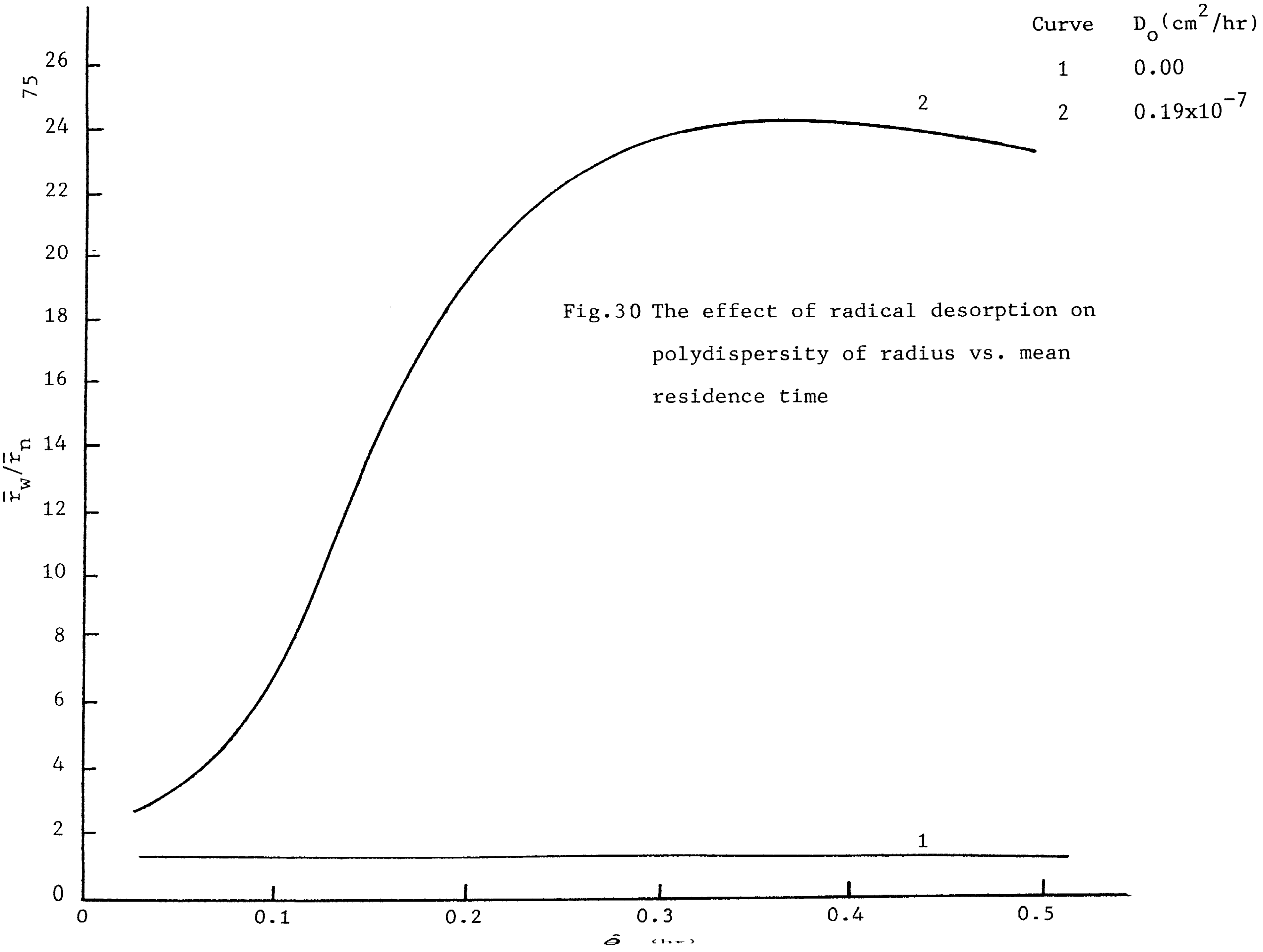


Fig.30 The effect of radical desorption on polydispersity of radius vs. mean residence time

Fig.31 The effect of the level of initiator on number and weight average radii at $\hat{\theta}$ =0.5(hr) and $D_o = 0.19X10^{-7}(cm^2/hr)$; $1I = 2.037X10^{-3}$(mole/ 1-H_2O)

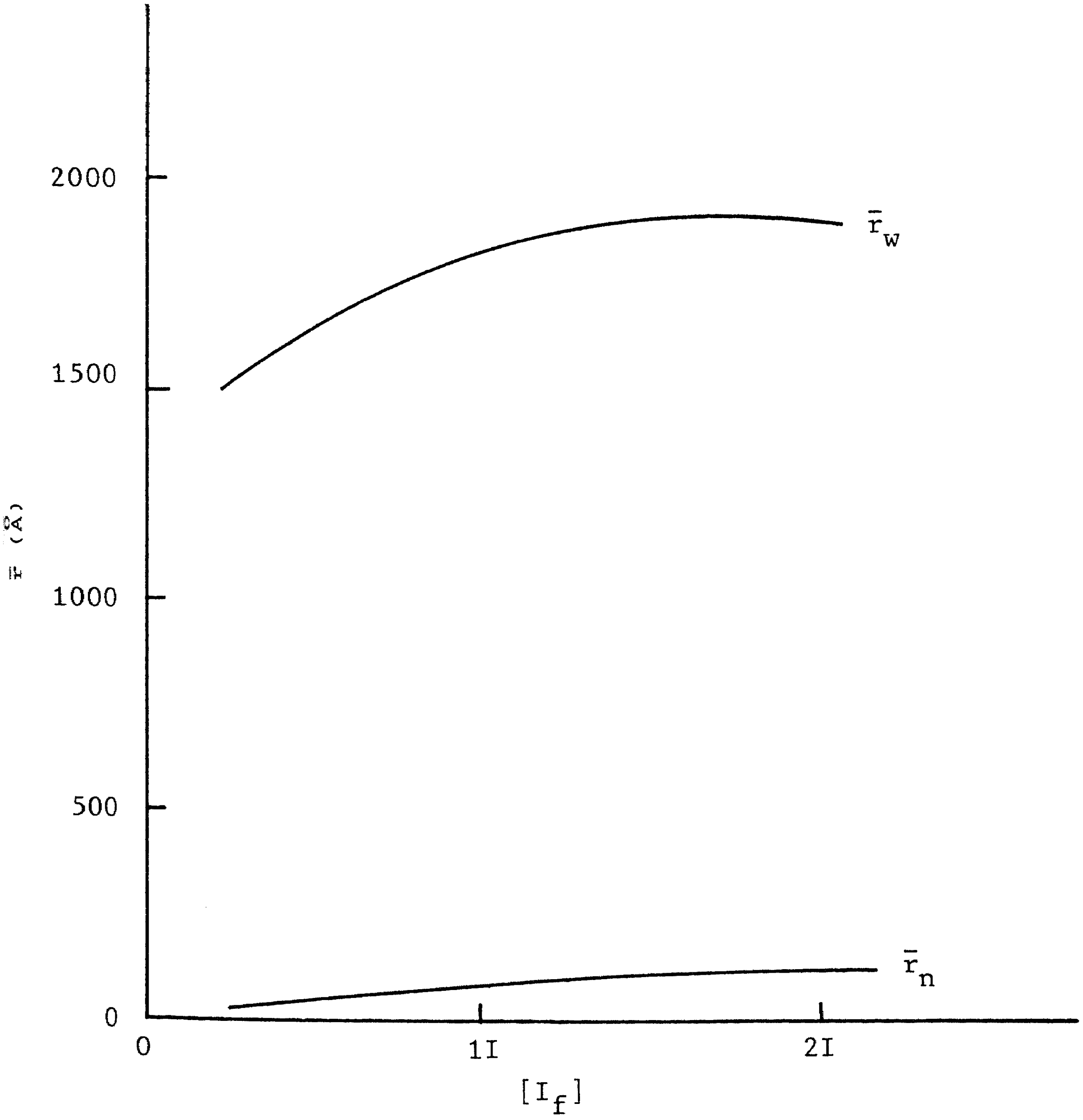
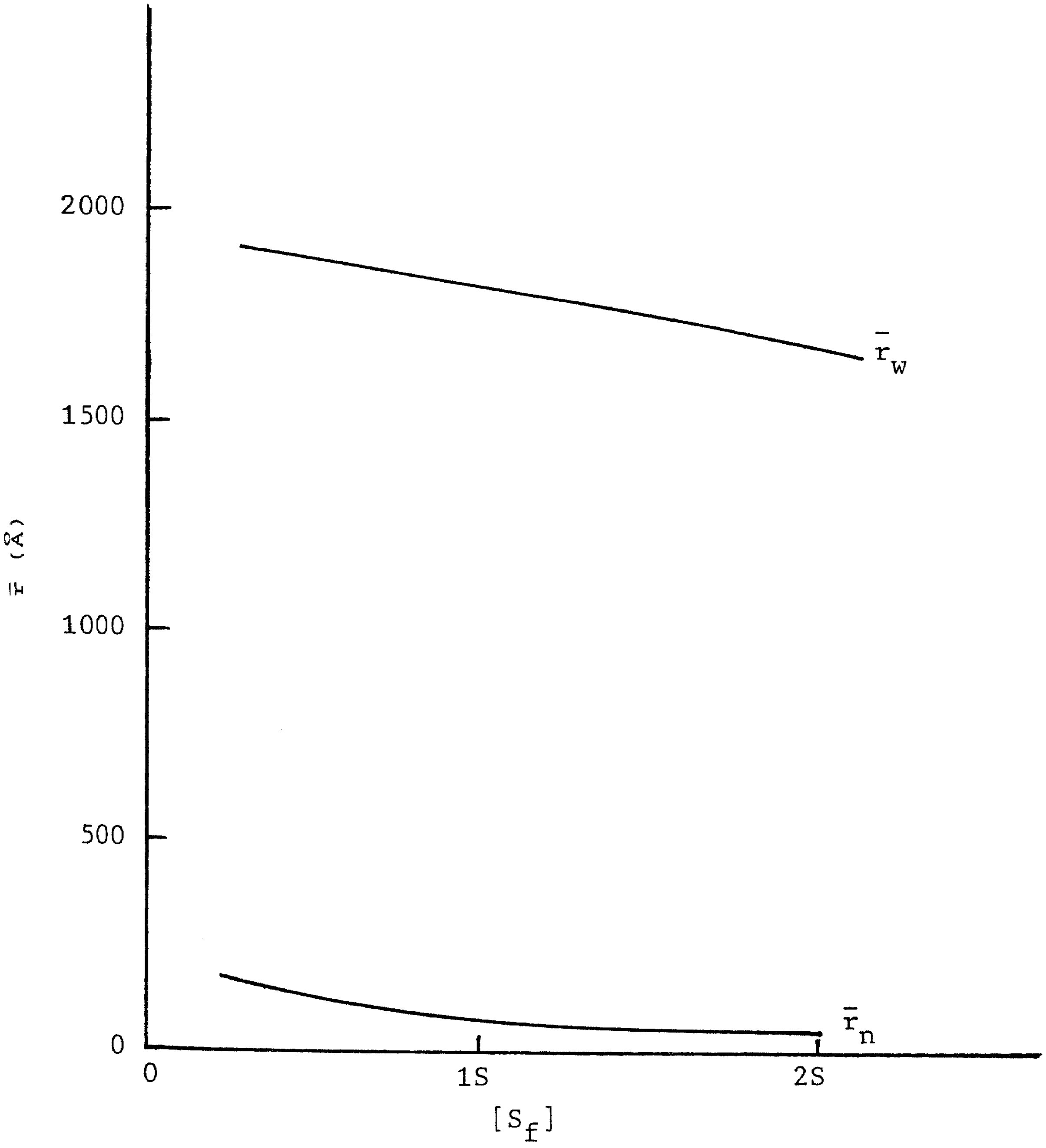


Fig.32 The effect of the level of emulsifier on number and weight average radii at $\hat{\theta}$ = 0.5(hr) and D_o=0.19X10^{-7}(cm^2/hr); 1S = 0.01736(mole/l-H_2O)



APPENDIX D

THE COMPUTER PROGRAM OF PARTICLE SIZE DISTRIBUTION FUNCTIONS

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C THIS PROGRAM IS MADE BY YING-YUH LU FOR SIMULATION OF A PARTICLE SIZE
C DISTRIBUTION IN CONTINUOUS EMULSION POLYMERIZATION OF VINYL ACETATE
C MONOMER.
C **********  NOTATION  **********
C DO   :PSEUDO-DESORPTION-COEFFICIENT (CM**2/HR)
C T    :MEAN RESIDENCE TIME IN CSTR (HOUR)
C RMP  :MONOMER CONCENTRATION IN POLYMER PARTICLES(MOLE/L OF PARTICLE)
C RIF  :INITIATOR CONCENTRATION IN FEED(MOLE/L-H2O)
C RMF  :MONOMER CONCENTRATION IN FEED(MOLE/L-H2O)
C RSF  :EMULSIFIER CONCENTRATION IN FEED(MOLE/L-H2O)
C RKP  :RATE CONSTANT FOR PROPAGATION(L/MOLE-HR)
C RKD  :RATE CONSTANT FOR INITIATOR DECOMPOSITION(1/HR)
C RKDF:RKD*F(1/HR)
C AM   :AREA OCCUPIED BY A SINGLE EMULSIFIER MOLECULES(CM**2/MOLECULE)
C DP   :DENSITY OF PLYMER(G/CM**3)
C DM   :DENSITY OF MONOMER(G/CM**3)
C RFM  :VOLUME FRACTION OF MONOMER IN PLYMER PARTICLE
C RF   :A SURFACE AFFINITY FACTOR TO ACCOUNT FOR THE RELATIVE EASE OF
C            RADICAL ENTRY INTO MICELLE VERSUS PLYMER PARTICLE
C RK   :GROWTH RATE CONSTANT,K (1/HR)
C R    :INITIATION RATE ,R (MOLE/L-HR)
C RMO  :INITIAL CONCENTRATION OF MICELLES(MOLE/L-H2O)
C RM   :RADIUS OF MICELLE (CM)
C B, C, D, EE:DIMENSIONLESS PARAMETERS,β,γ,α,φ
C XXX  :CONVERSION
C PERN:PERCENTAGE OF PLYMER PARTICLES WITH  VOLUME V IN SYSTEM
C ANS  :SYSTEM AVERAGE NUMBER OF RADICALS PER POLYMER PARTICLE
C TNT  :CONCENTRATION OF TOTAL POLYMER PARTICLES(MOLE/L)
C RN11:DIMENSIONLESS NUMBER DENSITY OF POLYMER PARTICLES WITH ONE
              FREE RADICAL AT SIZE    υ =1
C TRN1:DIMENSIONLESS CONCENTRATION OF TOTAL POLYMER PARTICLES WITH
             ONE FREE RADICAL
C TRN  :DIMENSIONLESS CONCENTRATION OF TOTAL POLYMER PARTICLES
C ARN  :NUMBER AVERAGE RADIUS(CM)
C ARW  :WEIGHT AVERAGE RADIUS(CM)
        READ(1,40) DO,T,RMP,RIF,RMF,RSF,RKP,RKD,RKDF,AM,DP
   40   FORMAT(E9.2,F6.3,F4.2,F9.7,F5.3,F7.5,E11.4,2F8.6,E9.2,F4.2)
        READ(1,50) DM,RFM,RF
   50   FORMAT(2F6.4,F3.1)
        RK=3.96565E-22*RKP*DM*RFM/(DP*(1.-RFM))
        R=2.*RKDF*RIF/(1.+RKD*T)
        RMO=RSF/100.
        RM=(100.*AM/12.56637)**.5
        B=RM*DO/RK
        D=R*(RM**3)/(RK*RMO)
        C=(RM**3)/(RK*T)
        EE=RMP*RMO*RKP*(RM**3)/(RMF*RK)
        WRITE(2,30) RK,R,RMO,RM,B,D,C,EE
   30   FORMAT(1X,'K=',E12.5,2X,'R=',E12.5,2X,'MO=',E12.5,2X,
       C'RM=',E12.5,2X,'B=',E12.5,2X,'D=',E12.5,2X,'C=',E12.5,2X,'EE=',
       CE12.5)
```

```
      M=3000
      CALL GUASS(B,C,D,M,RF,EE,RN11,TRN1,TRN,XXX,RM,ARN,ARW,CV)
      PDR=ARW/ARN
      ANS=TRN1/TRN
      TNT=RMO*TRN
      WRITE(2,10) DO,T,RN11,TRN1,TRN,ANS,TNT,XXX,ARN,ARW,CV,PDR
   10 FORMAT(1X,'TEMPERATURE= 50 C',/1X,'DESORPTION COEFFICIENT DO=',
     CE12.5,/1X,'RESIDENT TIME=',F5.2,/1X,'N1(1)=',E12.5,
     C/1X,'TOTAL DIMENSIONLESS NUMBER OF POLYMER PARTICLES WITH ONE FRE
     C RADICAL,TRN1=',E12.5,
     C/1X,'TOTAL DIMENSIONLESS NUMBER OF POLYMER PARTICLES, TRN=',E12.5
     C/1X,'AVERAGE NUMBER OF RADICALS PER POLYMER PARTICLE, NS=',E12.5,
     C/1X,'TOTAL CONCENTRATION OF POLYMER PARTICLES(MOLE/L-H2O)=',E12.5
     C/1X,'CONVERSION=',E12.5,
     C/1X,'THE NUMBER AVERAGE RADIUS(CM)=',E12.5,
     C/1X,'THE WEIGHT AVERAGE RADIUS(CM)=',E12.5,
     C/1X,'THE COEFFICIENT OF VARIABLE=',E12.5,
     C/1X,'THE POLYDISPERSITY OF RADIUS=',E12.5)
C V    :DIMENSIONLESS POLYMER PARTICLE VOLUME
C RV   :REAL POLYMER PARTICLE VOLUME, CM**3
C RAD : REAL RADIUS OF POLYMER PARTICLE (CM)
C RN1  :DIMENSIONLESS NUMBER DENSITY OF POLYMER PARTICLE WITH ONE FREE
C       RADICAL (RN1 IS THE SAME AS N1 USED IN ANSOWER SHEET)
C RN   :RN1+RNO (RN IS THE SAME AS N USED IN ANSOWER SHEET)
C RNV  :DIMENSIONLESS POLMER PARTICLES CONCENTRATION
C       (RNV IS THE SAME AS VN USED IN ANSOWER SHEET)
C RRNV:REAL POLYMER PARTICLES CONCENTRATION (MOLE/L-H2O)
C       (RRNV IS THE SAME AS RNV USED IN ANSOWER SHEET)
      DD=D/C
      RM3=RM**3
      V=0.
      VI=1.
      DO 2 L=1,70
      V=V+VI
      RV=4.18879*V*RM3
      VV3=V**.3333
      RAD=RM*VV3
      VV6=V**.6667
      QQ=SQRT(DD)*(VV3-1.)/(1.+DD*VV3)
      RFV=3.*(C/DD)*(VV3-1.)-2.*C*(V-1.)-
     C3.*((C**2.5/D**1.5)+B/(DD**.5))*ATAN(QQ)
      RN1=RN11*EXP(RFV)
      RN=RN1*(C+B/VV6+2*D*VV6)/(C+D*VV6)
      RNV=V*RN
      RRNV=RNV*RMO
      PERN=(RNV/TRN)*100
      WRITE(2,20) V,RV,RAD,RN1,RN,RNV,RRNV,PERN
   20 FORMAT(1X,'V=',F9.0,1X,'RV=',E12.5,1X,'RA=',E12.5,1X,'N1=',E12.5,
     C1X,'N=',E12.5,1X,'VN=',E12.5,1X,'RNV=',E12.5,1X,'PERN=',E12.5)
      IF(L.LT.10) GO TO 2
      VI=10
      IF(L.LT.19) GO TO 2
```

```
      VI=100
      IF(L.LT.28) GO TO 2
      VI=1000
      IF(L.LT.37) GO TO 2
      VI=10000
      IF(L.LT.46) GO TO 2
      VI=100000
      IF(L.LT.55) GO TO 2
      VI=1000000
    2 CONTINUE
      STOP
      END
      SUBROUTINE GUASS(B,C,D,M,RF,EE,RN11,TRN1,TRN,XXX,RM,ARN,ARW,CV)
C THE GAUSSIAN QUADRATURE (FOURTH ORDER) INTEGRATING METHOD
      T1=-.86113631
      T2=-.33998104
      W1=.34785485
      W2=.65214515
      D1=(D/C)**.5
      C1=3.*C**2
      P=3.*((C**2.5)/(D**1.5)+B*(C**.5)/(D**.5))
      SUM=0.
      XSUM=0.
      AREA=0.
      AREA1=0.
      AREA2=0.
      AREA3=0.
      AREA4=0.
      BB=1
      JJ=1
      DO 1 I=1,M
      A=BB
      BB=A+JJ
      P1=(A+BB)/2.
      P2=(BB-A)/2.
      X1=P1+P2*T1
      X2=P1+P2*T2
      X3=P1-P2*T2
      X4=P1-P2*T1
      X13=X1**.3333
      X23=X2**.3333
      X33=X3**.3333
      X43=X4**.3333
      X16=X1**.6667
      X26=X2**.6667
      X36=X3**.6667
      X46=X4**.6667
      Q1=D1*(X13-1.)/(1.+(D/C)*X13)
      Q2=D1*(X23-1.)/(1.+(D/C)*X23)
      Q3=D1*(X33-1.)/(1.+(D/C)*X33)
      Q4=D1*(X43-1.)/(1.+(D/C)*X43)
      RFV1=-2*C*(X1-1.)+C1*(X13-1.)/D-P*ATAN(Q1)
```

```
      RFV2=-2*C*(X2-1.)+C1*(X23-1.)/D-P*ATAN(Q2)
      RFV3=-2*C*(X3-1.)+C1*(X33-1.)/D-P*ATAN(Q3)
      RFV4=-2*C*(X4-1.)+C1*(X43-1.)/D-P*ATAN(Q4)
C RFV1,2,3,4 : F(V**3)
C CALCULATE THE DIMENSIONLESS CONCENTRATION OF TOTAL PARTICLES WITH
C ONE FREE RADICAL, TRN1, AND CALCULATE THE CONVERSION OF THE REACTION
      ERFV1=EXP(RFV1)
      ERFV2=EXP(RFV2)
      ERFV3=EXP(RFV3)
      ERFV4=EXP(RFV4)
      XSUM=XSUM+P2*(W1*(ERFV1+ERFV4)+W2*(ERFV2+ERFV3))
C XSUM=TRN1/N1(1)
C CALCULATE THE DIMENSIONLESS NUMBER DENSITY OF POLYMER PARTICLE WITH
C ONE FREE RADICAL AT PARTICLE SIZE EQUAL TO 1, N1(1)=RN11
      Y1=((C+RF*D*X16)/(RF*(C+D*X16)))*
     C(C/D+2.*X16+B/(D*X16))*ERFV1
      Y2=((C+RF*D*X26)/(RF*(C+D*X26)))*
     C(C/D+2.*X26+B/(D*X26))*ERFV2
      Y3=((C+RF*D*X36)/(RF*(C+D*X36)))*
     C(C/D+2.*X36+B/(D*X36))*ERFV3
      Y4=((C+RF*D*X46)/(RF*(C+D*X46)))*
     C(C/D+2.*X46+B/(D*X46))*ERFV4
      SUM=SUM+P2*(W1*(Y1+Y4)+W2*(Y2+Y3))
C SUM=1/N1(1)
C CALCULATE THE DIMENSIONLESS CONCENTRATION OF TOTAL PARTICLES,TRN
      YY1=((C+B/X16+2.*D*X16)/(C+D*X16))*ERFV1
      YY2=((C+B/X26+2.*D*X26)/(C+D*X26))*ERFV2
      YY3=((C+B/X36+2.*D*X36)/(C+D*X36))*ERFV3
      YY4=((C+B/X46+2.*D*X46)/(C+D*X46))*ERFV4
      AREA=AREA+P2*(W1*(YY1+YY4)+W2*(YY2+YY3))
C AREA=TRN/N1(1)
C
C CALCULATE $\int_{1}^{\infty} \upsilon N(\upsilon^{3})d(\upsilon^{3})$= WW1
C
      Y1Y=X13*YY1
      Y2Y=X23*YY2
      Y3Y=X33*YY3
      Y4Y=X43*YY4
      AREA1=AREA1+P2*(W1*(Y1Y+Y4Y)+W2*(Y2Y+Y3Y))
C AREA1 = WW1/N1(1)
C
C CALAULATE $\int_{1}^{\infty} \upsilon^{2} N(\upsilon^{3})d(\upsilon^{3})$ = WW2
C
      Y1YY=X16*YY1
      Y2YY=X26*YY2
      Y3YY=X36*YY3
      Y4YY=X46*YY4
      AREA2=AREA2+P2*(W1*(Y1YY+Y4YY)+W2*(Y2YY+Y3YY))
C AREA2 = WW2/N1(1)
C
C CALCULATE $\int_{1}^{\infty} \upsilon^{3} N(\upsilon^{3})d(\upsilon^{3})$= WW3
C
```

```
      YY1Y=X1*YY1
      YY2Y=X2*YY2
      YY3Y=X3*YY3
      YY4Y=X4*YY4
      AREA3=AREA3+P2*(W1*(YY1Y+YY4Y)+W2*(YY2Y+YY3Y))
C AREA3 = WW3/N1(1)
C                ∞ 4    3     3
C CALCULATE  ∫   υ N( υ )d( υ )= WW4
C             1
      YYY1=X1*X13*YY1
      YYY2=X2*X23*YY2
      YYY3=X3*X33*YY3
      YYY4=X4*X43*YY4
      AREA4=AREA4+P2*(W1*(YYY1+YYY4)+W2*(YYY2+YYY3))
C AREA4 = WW4/N1(1)
      IF(I.LT.10) GO TO 1
      JJ=10
      IF(I.LT.19) GO TO 1
      JJ=20
      IF(I.LT.200) GO TO 1
      JJ=100
      IF(I.LT.500) GO TO 1
      JJ=1000
      IF(I.LT.1500) GO TO 1
      JJ=10000
    1 CONTINUE
      RN11=1./SUM
      TRN1=RN11*XSUM
      XXX=(EE/C)*TRN1
      TRN=RN11*AREA
      ARN=RM*AREA1/AREA
      ARW=RM*AREA4/AREA3
      CV=(AREA2*AREA/(AREA1**2)-1.)**0.5
      RETURN
      END
```

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NOTATION

a : Area occupied by single emulsifier molecule(cm^2/molecule)

A_p : Dimensionless total surface area of polymer particles

$\hat{A}_p$: Dimensional total surface area of polymer particles (cm^2/l-H_2O)

A_s : Dimensionless total surface area of micelles plus particles

$\hat{A}_s$: Dimensional total surface area of micelles plus particles (cm^2/l-H_2O)

CMC : Critical micelle concentration (mole/l-H_2O)

D_o : Pseudo-desorption-coefficient

f : Efficiency of initiator

$[I_f]$: Initiator concentration in feed (mole/l-H_2O)

k_d : Rate constant of initiator decomposition (hr^{-1})

k_f : Rate of radical desorption from polymer particle (hr^{-1})

k_p : Rate constant of propagation (l/mole-hr)

$[M_f]$: Monomer concentration in feed (mole/l-H_2O)

$[M_p]$: Monomer concentration in polymer particle (mole/l-H_2O)

m_o : Initiator concentration of micelles (mole/l-H_2O)

N_{av} : Avogadro's number

N_i : Dimensionless number density of polymer particles with i free radicals

$\hat{N}_i$: Dimensional number density of polymer particles with i free radicals (mole/l-$H_2O \cdot cm^3$)

$\hat{N}$: Total number density of polymer particles(mole/l-$H_2O \cdot cm^3$)

$\hat{N}_T$: Concentration of total polymer particles (mole/l-H_2O)

$\hat{N}_{Tf}$: Concentration of total polymer particles in feed (mole/l-H_2O)

$\bar{n}$: The fraction of active polymer particle at a given size

$\bar{n}_s$: System average number of radicals per polymer paticles

R : The formation rate of initiator radical(mole/hr·l-H_2O)

r : Radius of polymer particle (cm)

r_m : Radius of micelle (cm)

$[S_f]$: Emulsifier concentration in feed (mole/l-H_2O)

X : Conversion

$\hat{\theta}$: Mean residence time (hr)

ρ_m : Density of monomer (g/cm^3)

ρ_p : Density of polymer (g/cm^3)

ϕ_M : Volume fraction of monomer in polymer particle

η : A surface affinity factor to account for the relative ease of radical entry into micelles versus polymer particles