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Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

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KINETICS OF AQUEOUS POLYSULFIDE SOLUTIONS: PART I. THEORY OF COUPLED ELECTROCHEMICAL AND CHEMICAL REACTIONS, RESPONSE TO A POTENTIAL STEP

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* This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Energy Storage and Distribution of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

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Kinetics of Aqueous Polysulfide Solutions: Part I. Theory of Coupled Electrochemical and Chemical Reactions, Response to a Potential Step

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January 1986

Abstract

The equations and assumptions that allow the derivation of the analytic form of the current transient for a small potential step are discussed. The equations are generalized so that they are applicable to the electrode reaction: $s_oO + ne^- \rightleftarrows s_rR$ where s_o and s_r are not necessarily equal. Then a system with a homogeneous reaction in solution coupled to the electrode reaction is considered. The treatment includes the case of a solution-phase homogeneous reaction that takes place at a rate comparable to that of the heterogeneous reaction. The current response to a potential step in the linear overpotential region is solved numerically for both a first-order homogeneous reaction and a homogeneous reaction involving dissociation-dimerization. Using this model the exchange current density and diffusion parameter of the heterogeneous reaction can be determined as cant the rate constants of the homogeneous reaction. It is shown that there is a range of parameters where the electrode current response is most sensitive to the values of the homogeneous rate data are discussed. the results for the two homogeneous kinetic models are qualitatively similar but differ quantitatively.

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Introduction

Many electrode reactions of technological interest are multi-step combinations of elementary chemical and electrochemical reactions. For design purposes it is necessary to determine species concentrations, exchange current densities and homogeneous kinetic parameters. If the solvent does not decompose and the electrode reaction and mechanism do not change over a sufficiently wide range of potential then there are several well-developed techniques for determining these parameters (1-3). However, techniques such as sweep voltammetry yield useful information only at potentials far from the equilibrium potential.

Energy conversion and storage devices (such as batteries) typically operate at low overpotentials in order to maximize energy efficiency and they often use electrolytes that are concentrated mixtures of several species. These characteristics suggest the use of DC relaxation techniques (such as current and potential step) which can often be used to obtain both diffusion and kinetic information in the low-overpotential region. Nagy (4) has recently analyzed the applicability of these techniques and determined the maximum measurable rate constants.

One of the key assumptions employed in the derivation of the analytic current-time transient for small potential steps is the existence of only one rate-determining step. The reaction sequence considered in this paper has two slow steps which occur at comparable rates. One of the rate-determining steps is a homogeneous reaction that occurs in the bulk solution. The other slow step is part of a multi-step electron transfer sequence at the electrode. The homogeneous rate constants, the exchange current density, and the diffusion parameter can be determined by fitting current-time transients to experimental data. Part I of this work discusses the effect of the homogeneous reaction rate on the current response at the electrode as well as the range of parameter values that can be determined. Part II of this work (5) makes use of this analysis to determine homogeneous rate constants, heterogeneous rate constants and species concentrations in the aqueous polysulfide redox system.

Background and Formulation of the Problem

Before the potential step is applied, the solution is at a uniform composition. At t=0, a small potential step (versus a reference electrode) is applied. A one-dimensional geometry is assumed with the x coordinate denoting the distance from the working electrode surface. If at the working electrode the multi-step electrode reaction[1]

$$s_oO + ne^- \rightleftarrows s_rR \tag{1}$$

takes place the current will follow the transient given by (4,6,7)

$$i = W\exp(\lambda^2 t)\,\mathrm{erfc}\,(\lambda t^{1/2}) \tag{2}$$

if the following assumptions hold:

1. The electrolyte is well-supported
2. Reaction 1 has only one rate-determining step
3. No diffusion of intermediates into the bulk occurs
4. No strong specific adsorption is present
5. Rise of the potential across the double layer is fast
6. Non-faradaic processes do not contribute significantly to the total current.

In the linear overpotential region W and λ have the following definitions:

$$W = \frac{V}{R_s + R_r} \tag{3}$$

$$\lambda = \frac{i_o}{\nu nF} \cdot \frac{R_r}{R_s+R_r}\left(\frac{s_o^2}{D_o^{1/2}C_{ob}} + \frac{s_r^2}{D_r^{1/2}C_{rb}}\right) \tag{4}$$

The diffusion parameter, $\left(\frac{s_o^2}{D_o^{1/2}C_{ob}}+\frac{s_r^2}{D_r^{1/2}C_{rb}}\right)$ and $\frac{i_o}{\nu}$ can be determined from W and λ. Before deriving the equations for the reaction sequence of concern in this paper, it is useful to examine the assumptions and equations that allow the simple analytical expression, Equation 2, to be derived.

Assumptions 1 and 3 allow a simplification of the material balance and flux equations and assumptions 2 and 4 are consistent with the assumed form of the electrode kinetic expression.

---

[1]Other species can participate in the electrode reaction. Their concentrations are assumed to be higher than those of O and R and they therefore do not contribute to the concentration overpotential. The reaction given here and the equations derived represent a generalization of the reaction $O + ne^- \rightleftarrows R$ where the overall stoichiometric coefficients are not necessarily equal.

The flux equation for dilute solutions can be written (8):

$$N_i = -z_i u_i F c_i \nabla\Phi - D_i \nabla C_i + C_i \mathbf{v} \tag{5}$$

Since convection is not expected to play a role at very short times, the last term of Equation 5 can be eliminated. The first term on the right hand side of Equation 5 is transport of ions by migration in the electric field. Only if assumption 1 holds can this term be eliminated. The material balance for species O or R can then be written:

$$\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial x^2} \tag{6}$$

If Reaction 1 has only one rate-determining step[2] and it is assumed that none of the intermediates are strongly adsorbed then the relation between current density and surface overpotential is:

$$i = i_o' \left\{ \exp\left[\frac{\alpha_a F \eta_a}{RT}\right] - \exp\left[\frac{-\alpha_c F \eta_a}{RT}\right] \right\} \tag{7}$$

This is the multi-step Butler-Volmer equation. The transfer coefficients and the reaction orders are related to the stoichiometry of Reaction 1 and the stoichiometric number by (9,10,11):

$$\alpha_a + \alpha_c = n/\nu \tag{8a}$$

$$z_{oc} - z_{oa} = s_o \tag{8b}$$

$$z_{ra} - z_{rc} = s_r \tag{8c}$$

The exchange current density, i_o', contains the *surface* concentrations of species O and R:

$$i_o' = \text{const} \cdot C_o^{(z_{oa}/\nu - s_o \alpha_a/n)} \Big|_{x=0} C_r^{(z_{ra}/\nu - s_r \alpha_a/n)} \Big|_{x=0} \tag{9}$$

The constant in Equation 9 is independent of the concentration of O and R, but depends on the rate constant of the rate-determining step and the equilibrium constants of the quasi-reversible steps (9,10). The relationship between the transfer coefficients, α, and the mechanism of the overall reaction has been discussed by Bockris, *et al.* (9,10).

[2]The other steps in the electrode reaction are assumed to be in quasi-equilibrium.

The concentration overpotential in a well-supported electrolyte is:

$$\eta_c = \frac{RT}{nF}\left(s_o \ln\left[\frac{C_o \mid_{x=0}}{C_{ob}}\right] - s_r \ln\left[\frac{C_r \mid_{x=0}}{C_{rb}}\right]\right) \tag{10}$$

Equation 10 neglects a small term which is of the order of the reactant concentration divided by the supporting electrolyte concentration (8). In addition, activity coefficient variations between the bulk and surface of the electrode are ignored.

Equations 7-10 can be combined (11) to give:

$$\begin{aligned} i = i_o \Bigg\{ & \left(\frac{C_r \mid_{x=0}}{C_{rb}}\right)^{z_{ra}/\nu} \left(\frac{C_o \mid_{x=0}}{C_{ob}}\right)^{z_{oa}/\nu} \exp\left[\frac{\alpha_a F(\eta_a+\eta_c)}{RT}\right] \\ & - \left(\frac{C_o \mid_{x=0}}{C_{ob}}\right)^{z_{oc}/\nu} \left(\frac{C_r \mid_{x=0}}{C_{rb}}\right)^{z_{rc}/\nu} \exp\left[\frac{-\alpha_c F(\eta_a+\eta_c)}{RT}\right] \Bigg\} \end{aligned} \tag{11}$$

In Equation 11, i_o contains the *bulk* concentrations of O and R. If the size of the potential step is sufficiently small then Equation 11 can be linearized (11):

$$i = \frac{nFi_o}{\nu RT}\left(\eta_a + \eta_c - \frac{RT}{nF}\left[s_o\left\{\frac{C_o \mid_{x=0}}{C_{ob}} - 1\right\} - s_r\left\{\frac{C_r \mid_{x=0}}{C_{rb}} - 1\right\}\right]\right) \tag{12}$$

The conditions under which this linearization is valid for dc relaxation techniques has been discussed by Nagy (14).

Three additional equations are needed to derive Equation 2. A voltage balance between the working and reference electrode:

$$V - E_{eq} = iR_s + \eta_a + \eta_c \tag{13}$$

a relation between the faradaic current[3] and species flux:

$$i = -\frac{nFD_o}{s_o}\frac{\partial C_o}{\partial x}\bigg|_{x=0} \tag{14}$$

and a relation between the fluxes of O and R at the surface:

$$\frac{D_o}{s_o}\frac{\partial C_o}{\partial x} + \frac{D_r}{s_r}\frac{\partial C_r}{\partial x} = 0 \tag{15}$$

Equation 2 is the solution to Equation 6 (for species O and R) subject to Equations 12-15 and the

[3]Anodic current and overpotentials are taken to be positive.

boundary conditions of semi-infinite linear diffusion. It is applicable after the non-faradaic current due to the charging of the double layer has decayed to a small value ($\approx 4R_sC_{dl}$). The maximum time of observation is set by the decreasing amount of kinetic information as time increases (the total overpotential is dominated by concentration rather than activation overpotential as time increases). At longer times, natural convection may also influence the current.

Nagy (12) has derived a form of Equation 2 where assumption 5 can be relaxed. In this case the equation obtained is similar to Equation 2, but it contains an additional parameter-- the rise time of potential across the double layer. Under certain conditions (4) neglecting this can lead to considerable error in the determination of the exchange current density. Nagy has also considered the case where both faradaic and non-faradaic contributions to the current are taken into account explicitly (4).

Equation 2 is also applicable in the non-linear overpotential range, but then W and λ will not have the meanings given by Equations 3 and 4 and uncompensated solution resistance cannot be taken into account explicitly (*cf.* Bard (13) and Macdonald (3)). Nagy (14) has considered the case where an equation similar to Equation 11 replaces Equation 12 and has accounted for the uncompensated resistance. A numerical solution is required. Where the parameters are determined by a non-linear least squares fit (for example MINPACK-1 (15)), substantially more computer time is needed for this case than for the linear case. Holub (16) and Susbielles (17) consider the linear overpotential case where specific adsorption cannot be neglected. In that case the electrode kinetic expression needs to be modified to take into account surface excess charge. They obtain an equation that is similar to Equation 2, but has extra terms that account for this specific adsorption.

Macdonald (3) presents a solution for a coupled chemical-electrochemical reaction where the overpotential is large enough so that the electrochemical reaction is under diffusion control only. The concentration of species O at the electrode surface is zero. The homogeneous kinetic parameters can be obtained from the current transient, but no information about the electrochemical kinetics can be derived under these conditions.

In this paper, we consider the case of Reaction 1 coupled to a homogeneous chemical reaction which occurs at a rate comparable to that of Reaction 1. The potential step is small enough to make Equation 12 valid. Table I shows the reaction sequence for two homogeneous kinetic cases. In Case I the homogeneous reaction is first order. In Case II it follows dissociation-dimerization kinetics. These reactions may be multi-step so long as the overall kinetics correspond to one of these cases.

The chemical reactions can be accounted for explicitly by adding the homogeneous reaction terms shown in Table I to Equation 6. For Case I this leads to a set of linear equations; for Case II some of the equations are non-linear. The following electrode reaction is considered to obey the assumptions that make the multi-step Butler-Volmer equation valid. The set of boundary conditions for the problems are completed by specifying that species Y is electro-inactive in the potential range of interest.

For ease of solution and interpretation it is desirable to make the equations and boundary conditions dimensionless. The parameters W and λ as defined by Equations 3 and 4 are used in the non-dimensionalization. These are the parameters that would be derived if the preceding chemical reaction was not a factor. Table II shows the definitions of the dimensionless groups and variables. Table III lists the dimensionless form of the material balances, initial conditions and boundary conditions. For the solutions presented in this paper, the diffusion coefficients of all species are set equal as are the stoichiometric coefficients. Then only the first four groups in the first column of Table II will affect the i^* vs. t^* curves.

The sets of parabolic partial differential equations were solved by casting them into finite difference form. Central difference approximations, with a truncation error $O(\Delta x^2)$, were used to approximate the space derivatives and the Crank-Nicolson implicit method was used to average the time derivative (18). This method is stable for all finite, positive values of $\Delta t/\Delta x^2$. In Case II the equations are non-linear. They were linearized about a trial solution so that only linear sets of finite difference equations needed to be solved (8). The BAND program, developed by Newman (8,19), was used to set up the matrix arrays.

Results and Discussion

There are four parameters to be determined from a set of experiments: the exchange current density and diffusion parameter that characterize the electrochemical reaction and the forward and backward rate constants that characterize the chemical reaction[4]. The values of the first four dimensionless groups in Table II plus the time interval of observation will determine the type of information obtainable for a given system.

We will use an example to illustrate the effect of a slow homogeneous reaction on the current-time response at an electrode. The electrochemical system is characterized by the parameters listed in the first column of Table IV. The square points in Figure 1 were calculated from the numerical model (first-order kinetics). The limiting cases of no coupled homogeneous reaction (k_f=0, solid line) and very fast homogeneous reaction ($k_f \rightarrow \infty$, dotted line) are shown. The current-time responses for these limiting cases are calculated from Equation 2 using the diffusion parameters shown in the second column of Table IV. The diffusion parameter for the fast homogeneous reaction ($k_f \rightarrow \infty$) is obtained from Equation 4 by replacing C_{ob} with C_{yb}. The usual method of obtaining the kinetic and diffusion parameters is a non-linear least squares fit of the data to an assumed form of the current-time transient. The last column of Table IV shows the result of using Equation 2 to fit the data over three different time intervals. The dashed line in Figure 1 is the non-linear least squares fit for the time interval 0-3.5 milliseconds.

Since Equation 2 does not describe the current-time response of the system over the entire time interval, the values of exchange current density and diffusion parameter obtained from the least squares fit will depend on the time interval selected. This can result, for example, in calculated species concentrations that do not correspond to actual species concentrations in solution. The exchange current density is underestimated because of the "flattening" of the current-time transient at longer times.

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[4]If the equilibrium constant is known then only three parameters are adjustable because the rate constants are related by $Keq = \frac{k_f}{k_b}$.

At $t \rightarrow 0$ the homogeneous reaction does not influence the current response because the boundary layer thickness is zero. As time increases, the homogeneous reaction will have an increasingly important effect. The last column of Table IV shows the effect of changing the time interval over which the non-linear least squares fit to Equation 2 is carried out. The fit to the short-time data will give a calculated response at longer times that will be below the experimental currents, but will produce exchange current density and diffusion parameter values that approach those of the unperturbed electrode reaction. These values can then be used as starting values in a least-squares fit using the model that includes the slow homogeneous reaction, with data over the full time range.

It is useful to construct dimensionless working curves that can be used to determine the range of accessible rate constants and diffusional information. If a numerical simulation is carried out for Case I, and for a given C_{ob}/C_{rb}, k_f/λ^2 and K_{eq} but different values of V^*, all the curves will have the same shape. In fact, all the curves will collapse into one if $|i^*/V^*|$ is plotted versus t^*. The appendix of this paper shows why this behavior is expected. The cathodic and anodic responses, for potential steps of equal size, are mirror images of each other. For Case II, i^*/V^* will, in general, not be independent of V^*. However, under the conditions where the linearization of Equation 11 is valid, $|i^*/V^*|$ for different values of V^* do not deviate from each other by more than a few hundredths of a percent. In order to facilitate comparison among figures $i^*(1+C_{ob}/C_{rb})/V^*$ is plotted versus t^*. The $(1+C_{ob}/C_{rb})$ term is multiplied by i^*/V^* so that curves with different values of the group C_{ob}/C_{rb} will have the same value of intercept. These dimensionless working curves are presented in Figs. 2-4.

The case of most practical interest is where the electroactive species O is in much smaller concentration than species Y, and therefore K_{eq} is small. At small values of K_{eq} ($<\approx 10^{-4}$), the back reaction dominates and the shape of the current transient is determined by k_b/λ^2 and C_{ob}/C_{rb}. The group k_b/λ^2 is obtained by combining groups 3 and 4 from column 2 of Table II. Figures 2 and 3 show the dimensionless current transients for Case I and C_{ob}/C_{rb} of 0 and 1, respectively. The bottom curve in each figure shows the response when no preceding reaction

takes place (k_f=0). In Figure 2 the curves becomes almost flat as the homogeneous reaction rate increases because both Y and R are in excess. Only at short times is any transient behavior detectable. In Figure 3, O and R are present in small and equal quantities, and at high homogeneous reaction rates the concentration overpotential due to the depletion or production of R (depending on the sign of the potential step) dominates the shape of the current transient. There is a range of k_b/λ^2 where the response of the system is most sensitive to the homogeneous kinetics. For each curve there are values of t^* where homogeneous and heterogeneous kinetic parameters can be optimally determined.

If we imagine a system where some information is available on the exchange current density and species concentrations in the electrochemical reaction, then curves of the types shown in Figures 2 and 3 can be used to determine the range of measurable reaction rates for the homogeneous reaction and the time window needed for observation. Estimates of exchange current density and species concentrations allow λ to be calculated, and t^* can be transformed into a dimensional time. For each curve there is a interval in which the electrode response is not significantly influenced by the homogeneous reaction. A better estimate of W and λ using Equation 2 can be obtained in this interval. Using these estimates the full mathematical model can be used to fit the current response over the longer time range where the homogeneous reaction does significantly change the current response. The current response will be most sensitive to the values of the homogeneous rate constants in the middle range of the curves in Figures 2 and 3. This will be the region where this technique is most applicable.

If the homogeneous reaction scheme of Case II is considered at small values of K_{eq} the curves will be qualitatively similar to those for Case I. The groups that determine the current response at the electrode are k_bC_{ob}/λ^2 and C_{ob}/C_{rb}. Figure 4 shows the normalized current transients for the condition of $C_{ob}/C_{rb} = 0$. There is a quantitative difference in response for Case I and Case II, even when $k_bC_{ob}/\lambda^2 = k_b/\lambda^2$. The range of homogeneous rate constants for which the current response is most sensitive to the rate of the homogeneous reaction is also somewhat different.

Summary

The results presented here represent an extension of the small potential step technique to include reactions which have two slow steps, one of which is a homogeneous reaction in bulk solution. The material balances and boundary conditions are presented for homogeneous reactions following first-order kinetics or a dissociation-dimerization kinetics. At short times the current response at the electrode follows the current-time response given by Equation 2 (or modified versions of it (4)). Over a longer time interval a fit of experimental data to Equation 2 will give species concentrations and an exchange current density that are erroneous. Using the full numerical model, the correct diffusional and rate data for both homogeneous and heterogeneous reactions can be obtained. For a particular system the type of information that can be obtained will depend on the time available for observation and the values of the dimensionless groups listed in Table II. Figures 2-4 should be of help in determining the information obtainable for a given system.

Appendix

If the potential step can be simulated by a combination of linear partial differential equations (PDE's) and linear boundary conditions it will be shown that i^*/V^* is independent of V^*. This result will also apply to systems with no homogeneous reactions (Equation 2), and slow homogeneous reactions with zero- or first-order kinetics.

A set of linear PDE's and boundary conditions can be reduced to a set of ordinary differential equations and algebraic equations by a Laplace transform technique (20). From Equations III-1 and III-3 plus boundary conditions III-8 and II-9b we can obtain:

$$\overline{C}_o^* = A\overline{f}(s,x^*,\frac{k_f}{\lambda^2},K_{eq}) \tag{A-1}$$

From the transform of Equation III-2:

$$\overline{C}_r^* = B\overline{g}(s,x^*) \tag{A-2}$$

The constants A and B can be related by III-9a. Using that boundary condition and the relation between current density and concentration gradient (and assuming for illustrative purposes that all diffusion coefficients are equal and the stoichiometric coefficients are equal):

$$\bar{i}^* = \frac{-V^* \dfrac{\partial \bar{f}}{\partial x^*}}{s\left[\bar{f} - \dfrac{C_{ob}}{C_{rb}} \dfrac{\dfrac{\partial \bar{f}}{\partial x^*}}{\dfrac{\partial \bar{g}}{\partial x^*}} - \left(1 + \dfrac{C_{ob}}{C_{rb}}\right) \dfrac{\partial \bar{f}}{\partial x^*}\right]} \tag{A-3}$$

All the functions and derivatives in Equation A-3 are evaluated at $x^*=0$. The right hand side of Equation A-3 can be denoted by $\bar{h}$. The inverse transform of Equation A-3 can be taken:

$$\frac{i^*}{V^*} = h(t^*, C_{ob}/C_{rb}, k_f/\lambda^2, K_{eq}) \tag{A-4}$$

Therefore i^*/V^* is independent of V^*.

Acknowledgement

This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Energy Storage and Distribution of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

Nomenclature

Roman

C, concentration (mole/cm^3)

C_{dl}, double layer capacity (F/cm^2)

D, diffusion coefficient (cm^2/sec)

E_{eq}, rest potential of working electrode with respect to reference electrode (volts)

F, Faraday (96,487 C/equiv)

i, current density (A/cm^2)

i_o, exchange current density referenced to bulk concentrations (A/cm^2)

i_o', exchange current density referenced to surface concentrations (A/cm^2)

K_{eq}, equilibrium constant

k_f, forward rate constant (sec^{-1})

k_b, reverse rate constant (sec^{-1} or liters/mole-sec)

n, number of electrons

N, flux (mole/cm^2-sec)

R, gas constant (J/mole-K)

R_o, R_y, homogeneous reaction rates (mole/cm^3–sec)

R_s, uncompensated solution resistance (ohm-cm^2)

R_r, linear reaction resistance, $RT\nu/nFi_o$ (ohm–cm^2)

s, Laplace variable

s_o, s_r, stoichiometric coefficients for overall reaction

t, time (sec)

T, temperature (K)

u, mobility (cm^2–mole/J–sec)

V, potential difference between working and reference electrodes (volts)

W, defined by Equation 3 (A/cm^2)

x, distance from working electrode surface (cm)

z, multiple of electron charge

z_a, anodic reaction order

z_c, cathodic reaction order

Greek

α_a, α_c, transfer coefficients

η_a, activation overpotential (volts)

η_c, concentration overpotential (volts)

λ, defined by Equation 4 ($sec^{-1/2}$)

ν, stoichiometric number

Φ, potential (volts)

Subscripts

b, bulk

i, species i

o, species O

r, species R

y, species Y

Superscripts

*, dimensionless variable

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Table I. Reaction Schemes

Case I	Case II
1st Order Reaction	Dissociation-Dimerization Reaction
$Y \rightleftarrows O$	$Y \rightleftarrows 2O$
$s_oO + ne^- \rightleftarrows s_rR$	$s_oO + ne^- \rightleftarrows s_rR$
$R_o = -R_y = k_fC_y - k_bC_o$	$\frac{1}{2} R_o = -R_y = k_fC_y - k_bC_o^2$

Table II. Dimensionless Variables

Dimensionless Groups	Definitions
1. V^*	$V^* = \frac{nF}{RT}$
2. $\frac{C_{ob}}{C_{rb}}$	$t^* = \lambda^2 t$
3. K_{eq}, case I; $\frac{K_{eq}}{C_{ob}}$, case II	$x^* = \frac{\lambda x}{D_o^{1/2}}$
4. $\frac{k_f}{\lambda^2}$	$i^* = \frac{iV^*}{s_o W\left(1 + \frac{s_r^2 D_o^{1/2} C_{ob}}{s_o^2 D_r^{1/2} C_{rb}}\right)}$
5. $\frac{D_o}{D_r}$	$C_o^* = \frac{C_o}{C_{ob}}$
6. $\frac{D_o}{D_y}$	$C_r^* = \frac{C_r}{C_{rb}}$
7. $\frac{s_o}{s_r}$	$C_y^* = \frac{C_y}{C_{yb}}$

Table III. Dimensionless Equations

Case I	Case II
First-Order Reaction	Dissociation-Dimerization Reaction
Material Balances	Material Balances
$\frac{\partial C_o^*}{\partial t^*}=\frac{\partial^2 C_o^*}{\partial x^{*2}}+\frac{k_f}{K_{eq}\lambda^2}(C_y^*-C_o^*)$ (III-1)	$\frac{\partial C_o^*}{\partial t^*}=\frac{\partial^2 C_o^*}{\partial x^{*2}}+\frac{2k_f C_{ob}}{K_{eq}\lambda^2}(C_y^*-C_o^{*2})$ (III-4)
$\frac{\partial C_r^*}{\partial t^*}=\frac{D_r}{D_o}\frac{\partial^2 C_r^*}{\partial x^{*2}}$ (III-2)	$\frac{\partial C_r^*}{\partial t^*}=\frac{D_r}{D_o}\frac{\partial^2 C_r^*}{\partial x^{*2}}$ (III-5)
$\frac{\partial C_y^*}{\partial t^*}=\frac{D_y}{D_o}\frac{\partial^2 C_y^*}{\partial x^{*2}}-\frac{k_f}{\lambda^2}(C_y^*-C_o^*)$ (III-3)	$\frac{\partial C_y^*}{\partial t^*}=\frac{D_y}{D_o}\frac{\partial^2 C_y^*}{\partial x^{*2}}-\frac{k_f}{\lambda^2}(C_y^*-C_o^{*2})$ (III-6)

Initial Conditions

at $t^*=0$, $x^*\geq 0$: $C_o^*=1$, $C_r^*=1$, $C_y^*=1$ (III-7)

Boundary Conditions

as $x^*\rightarrow\infty$, $t^*\geq 0$: $C_o^*\rightarrow 1$, $C_r^*\rightarrow 1$, $C_y^*\rightarrow 1$ (III-8)

at $x^*=0$, $t^*\geq 0$:

$$\frac{\partial C_r^*}{\partial x^*}+\frac{D_o}{D_r}\frac{s_r}{s_o}\frac{C_{ob}}{C_{rb}}\frac{\partial C_o^*}{\partial x^*}=0 \quad \text{(III-9a)}$$

$$\frac{\partial C_y^*}{\partial x^*}=0 \quad \text{(III-9b)}$$

$$V^*=s_o(C_o^*-1)-s_r(C_r^*-1)-s_o\left[1+\frac{s_r^2 D_o^{1/2} C_{ob}}{s_o^2 D_r^{1/2} C_{rb}}\right]\frac{\partial C_o^*}{\partial x^*} \quad \text{(III-9c)}$$

Table IV. Parameters For Figure 1.

Reaction Parameters	Derived Quantities	Results of Fit to Equation 2
$i_o/\nu = 1$ mA/cm^2 $V = 12.8$ mV $n = 1$	$W = 0.5$ mA/cm^2 $V^* = 0.5$ $R_r = 0.5$ ohm–cm^2	$0<t<3.5$ ms $i_o/\nu = 0.73$ mA/cm^2 Diffusion Parameter = $1.09\text{x}10^9$ cm^2–sec$^{1/2}$/mole
$C_{ob} = 0.1$ mM $C_{rb} = 10$ mM $C_{yb} = 1$M	$\lambda = 33.1$ sec$^{-1/2}$ Diffusion Parameter = $3.2\text{x}10^9$ cm^2–sec$^{1/2}$/mole $k_b/\lambda^2 = 0.913$	$0<t<2$ ms $i_o/\nu = 0.83$ mA/cm^2 Diffusion Parameter = $1.66\text{x}10^9$ cm^2–sec$^{1/2}$/mole
$D = 10^{-5}$ cm^2/sec $K_{eq} = 10^{-4}$ $k_f = 0.1$ sec^{-1}	if $k_f \rightarrow \infty$ $\lambda = 0.331$ sec$^{-1/2}$ Diffusion Parameter = $3.2\text{x}10^7$ cm^2–sec$^{1/2}$/mole	$0<t<1$ ms $i_o/\nu = 0.92$ mA/cm^2 Diffusion Parameter = $2.26\text{x}10^9$ cm^2–sec$^{1/2}$/mole

List of Figures

Figure 1: □, calculated from numerical model using parameters in Table IV; _____, k_f=0; -----, least-squares fit of Equation 2 to points.

Figure 2: Case I kinetics, C_{ob}/C_{rb}=0, k_b/λ^2 as labeled.

Figure 3: Case I kinetics C_{ob}/C_{rb}=1, k_b/λ^2 as labeled.

Figure 4: Case II kinetics, C_{ob}/C_{rb}=0, k_bC_{ob}/λ^2 as labeled.

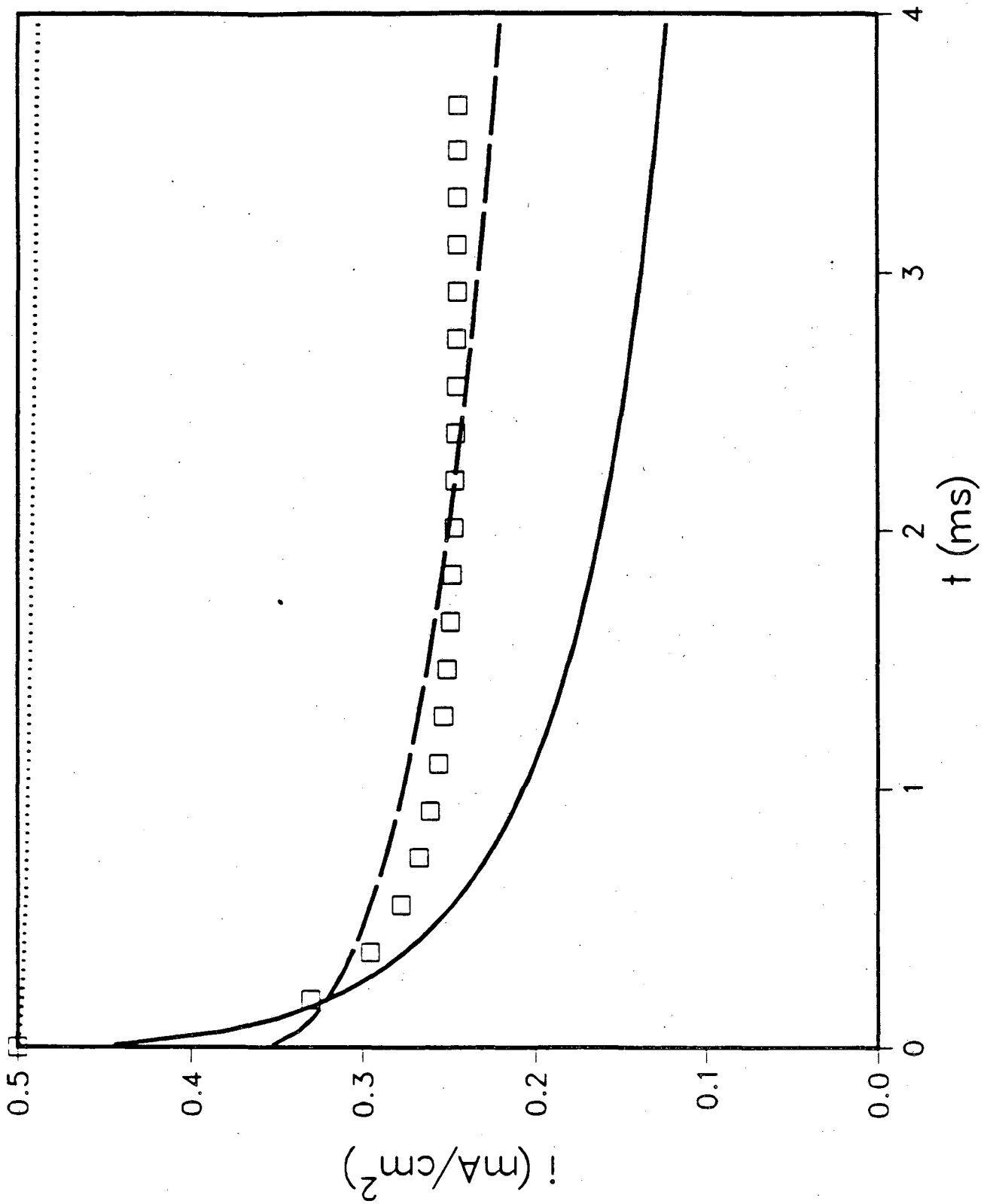

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Figure 1

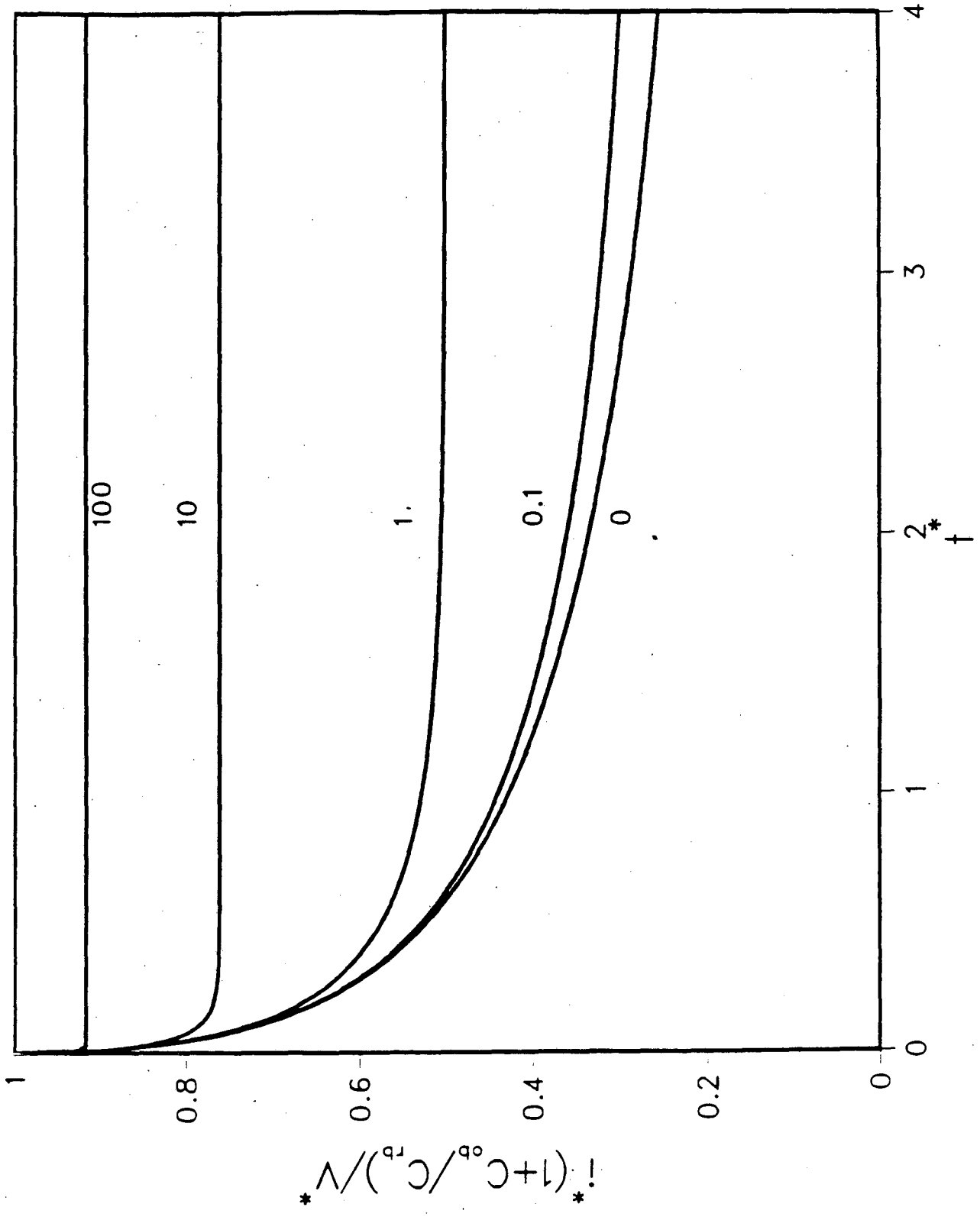

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Figure 2

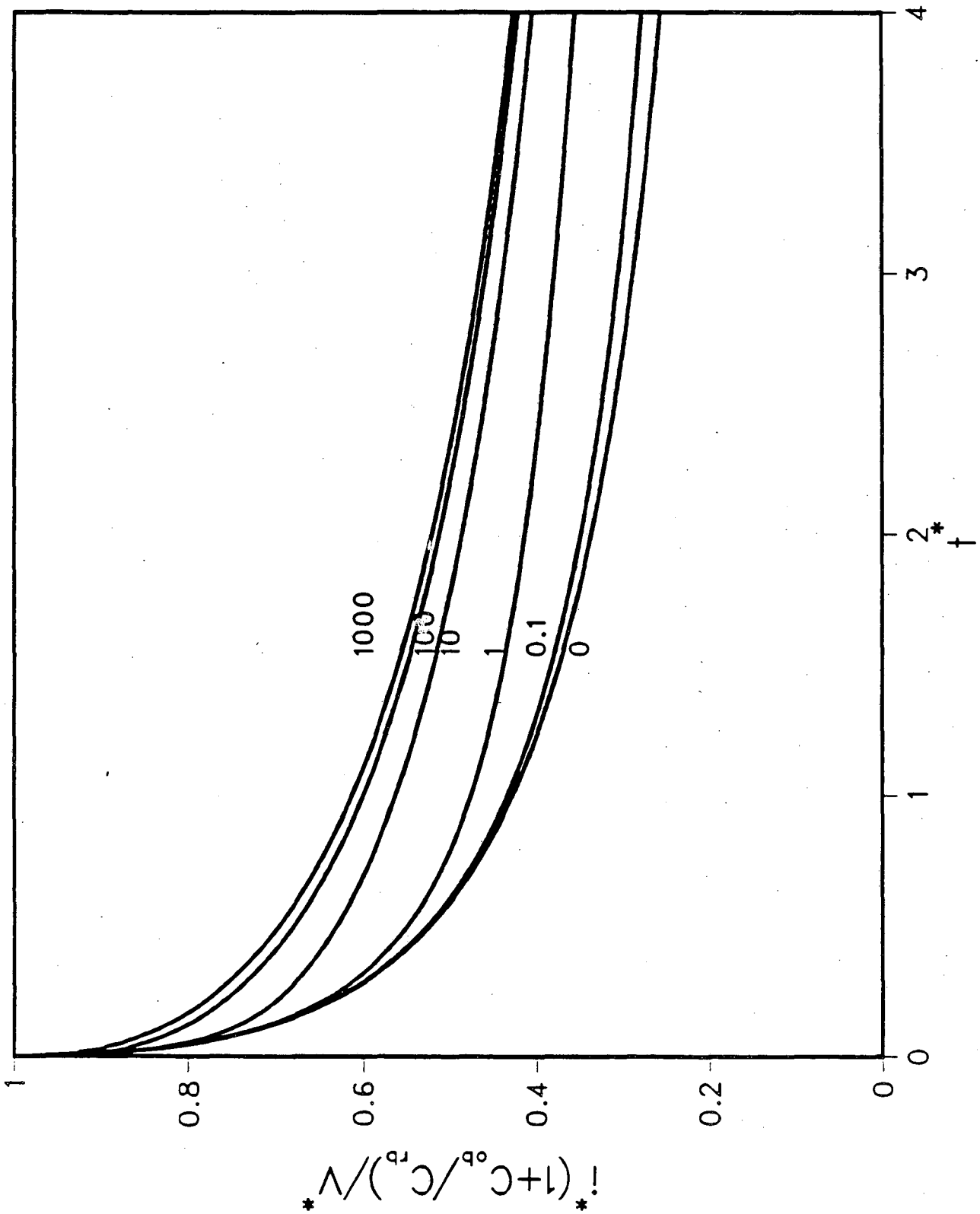

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Figure 3

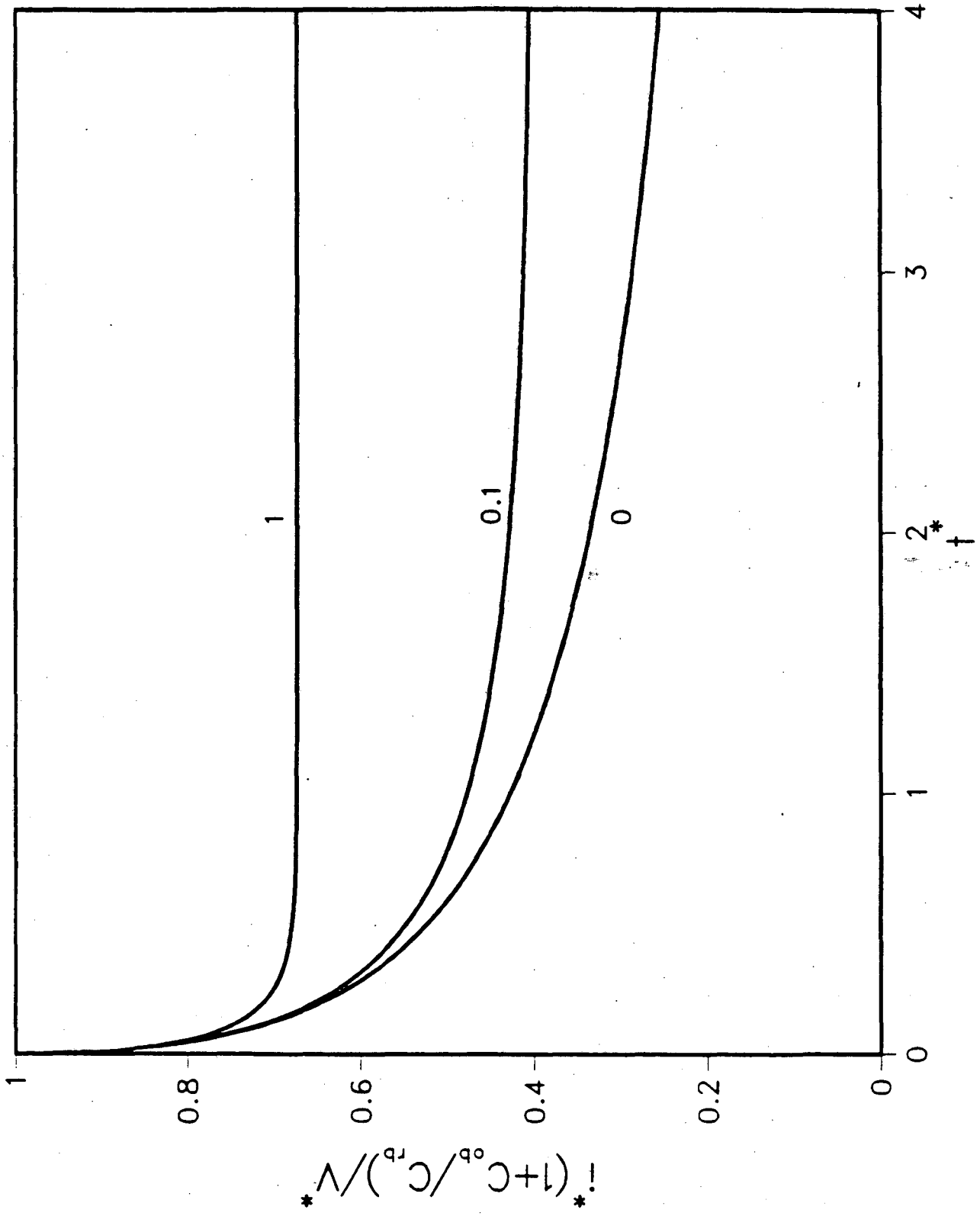

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Figure 4

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