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UNIVERSITÉ D'OTTAWA
UNIVERSITY OF OTTAWA

PREFACE

It will be useful to outline the structure of the thesis at first. The material is presented in four Chapters: Chapter 1 is an introductory review on previous work and discusses problems concerning the determination of the behaviour of adsorbed reaction intermediates at electrode surfaces and their relation to electrocatalysis in the hydrogen evolution reaction at various metal cathodes. Chapter 2 describes the experimental techniques and electrochemical systems employed in the present research. Chapter 3 presents the principles of the potential-decay and a.c. impedance methods that were used for the study of "overpotential-deposited" H in the H_2 evolution reaction while Chapter 4 reports the experimental results and discussion.

The work presented in this thesis has been published or is in course of publication, as follows:

1. Data Collection and Processing of Open-Circuit Potential-Decay Measurements Using a Digital Oscilloscope: Derivation of H-Capacitance Behaviour of H_2 -Evolving, Ni-based Cathodes, B.E. Conway, Lijun Bai and D.F. Tessier, *Electroanal. chem.*, 161 (1984) 39.
2. H_2 Evolution Kinetics at High Activity Ni-Mo Electrocoated materials and the State of Adsorbed H, B.E. Conway and Lijun Bai, *Proc. Fifth World Hydrogen Energy Conference*, Toronto, Canada, July, (1984) 879.

3. Determination of the Adsorption Behaviour of 'Overpotential-deposited' Hydrogen-atom Species in the Cathodic Hydrogen-evolution Reaction by Analysis of Potential-relaxation Transients, B.E. Conway and Lijun Bai, J. chem. Soc., Faraday Trans. 1, 81 (1985) 1841.
4. Determination of Adsorption of OPD H Species in the Cathodic Hydrogen Evolution Reaction at Pt in Relation to Electrocatalysis, B.E. Conway and Lijun Bai, J. Electroanal. chem., 198 (1986) 149.
5. Behaviour of Overpotential-deposited Species in Faradic Reaction; Part II: A.C. Impedance Measurements at Activated and Unactivated Pt Cathodes, Lijun Bai, D.A. Harrington and B.E. Conway, in course of publication.
6. Behaviour of Overpotential-deposited Species in Faradaic Reaction; Part III: A.C. Impedance Measurements at Ni and Ni-Mo-Cd Electrocoated Cathodes, Lijun Bai and B.E. Conway, in course of publication.

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ABSTRACT

A new method of analysis of the kinetics of the decay of overpotential on open-circuit, following interruption of a polarizing current, has been applied to the study of the adsorption behavior of the "overpotential-deposited" (o.p.d.) H, generated as the kinetically significant intermediate in the cathodic hydrogen evolution reaction (h.e.r.) at appreciable currents.

The a.c. impedance method has also been applied to the study of the adsorption behavior of the o.p.d. H, using a development of Armstrong's treatment for interpretation of the results. This gives, for the first time by this method, reliable information about the o.p.d. H, although the a.c. impedance method has been successfully employed to study the underpotential deposited (u.p.d.) H in other earlier work. The complementary use of the a.c. method gives results that can be compared with those derived using the potential decay method.

Results are described for the h.e.r. at Pt, Au, Ni and electro-deposited Ni-Mo-Cd composite cathode materials in acidic and/or alkaline solutions.

At Ni and Ni-Mo-Cd alloys the steady-state fractional H coverage approaches a limiting value, <1 , with increasing overpotential which can be explained by the kinetics of H deposition and desorption steps. At Au, the H coverage is very small but H surface diffusion is involved in the h.e.r. from acidic solution. At Pt, a dual H

desorption pathway is involved and, in acidic solution, some evidence of H sorption as a surface-region hydride is indicated and may be the reason for the excellent electrocatalytic behavior of active Pt for the h.e.r. in acidic solution.

Through information obtained by means of the above two methods, the adsorption behavior of the o.p.d. H and mechanistic information for the h.e.r. at these cathode materials can be quantitatively correlated and the current-voltage behavior rationalized. In particular, the Tafel-slope behavior for the h.e.r. under various conditions and for several cathode materials can be understood.

Chapter 1

INTRODUCTION

1.1 Introductory remarks

Despite its major importance in electrocatalysis and mechanistic aspects of electrode processes, the experimental determination of the adsorption behavior of kinetically involved intermediates, e.g. H in cathodic H_2 evolution, in electrode reactions proceeding at appreciable Faradaic currents, has hitherto remained little developed. This is a surprising situation.

A new method of analysis of the kinetics of the decay of overpotential on open-circuit, following interruption of a polarizing current, has been applied to the study of the adsorption behavior of the "overpotential-deposited" (o.p.d.) H, generated as a intermediate in the cathodic hydrogen evolution reaction (h.e.r.) at appreciable currents.

The a.c. impedance method has also been applied to the study of the adsorption behavior of the o.p.d. H, using a development of Armstrong's treatment for interpretation of the results. This gives, for the first time by this method, reliable information about the o.p.d. H although the a.c. impedance method has been successfully employed to study the underpotential deposited (u.p.d.) H in other earlier work¹. The complementary use of the a.c. method gives results that can be compared with those derived using the single transient, potential decay method developed in this laboratory.

Results are described for the h.e.r. at Pt, Au, Ni, and electrodeposited Ni-Mo-Cd composite cathode materials in acidic

and/or alkaline solution. Through information obtained by means of the above two methods, the adsorption behavior of the o.p.d. H and mechanistic information for the h.e.r. at these cathode materials are rationalized; in particular, the Tafel slope behavior for the h.e.r. under various conditions and for several cathode materials can be understood.

1.2 General kinetic aspects of electrode processes

In terms of usual general way of representing a reaction velocity, v , that of an electrochemical process can be written²⁻⁸, in terms of the current-density i , as:

$$i = nFv = \left\{ \tau (kT/h) \exp[-\Delta\bar{G}^\ddagger/RT] \right\} nF(C_R)_s (1-\theta) \quad (1.1)$$

where the rate constant according to absolute rate theory⁹ is given by the term in curly brackets, τ is the transmission coefficient (taken as approximately unity⁹), k , T and h have their usual significance and $\Delta\bar{G}^\ddagger$ is an electrochemical standard free energy of activation; nF is the number of coulombs involved (expressed in terms of Faradays) in the charge-transfer step of the reaction proceeding at the rate v mol s⁻¹ cm⁻²; $(C_R)_s$ is the surface concentration of the reactant molecule or ion and $(1-\theta)$ is a geometrical site availability factor giving the specific fractional area available for continuing discharge of species on the surface.

The coverage, θ , referring to the steady-state coverage of intermediates adsorbed on the surface, will be discussed in more detail later in the present thesis.

$\Delta\bar{G}^\ddagger$ is related to the chemical free energy of activation,

$\Delta G^\ddagger$, for an ordinary chemical reaction by the equation:

$$\Delta \bar{G}^{\circ \ddagger} = \Delta G^{\circ \ddagger} - \beta F(\Delta \phi_r + \eta) \quad (1.2)$$

This equation involves, in the second term on the r.h.s., an electrical energy factor comprised of the metal-solution potential difference, $\Delta \phi$, at the electrode interface given by the sum of $\Delta \phi_r$, the absolute metal-solution potential difference when the system is at equilibrium, plus an overpotential, η , required to drive the reaction at net current density, i . The quantity, β , is a barrier symmetry factor analogous to Brønsted's factor α in his linear free energy relation, since it represents the fraction of the electrical free energy provided to the system which is used to increase the reaction rate beyond its value when $\Delta \phi = 0$. It is commonly accepted, on both experimental and theoretical grounds, that the symmetry factor β should be close to one half for a more or less symmetrical energy barrier, and this value will be assumed in the subsequent discussion of kinetic parameters. The potentials $\Delta \phi$ and $\Delta \phi_r$ normally fall a thin interfacial region at the electrode surface, the double-layer.

Combining eqns. (1.1) and (1.2) for a simple discharge process, the net current i is given by eqn. (1.3) which leads, through eqn. (1.2), to a form of the Butler-Volmer equation:

$$\begin{aligned} i &= i_f - i_b \\ &= i_o \{ \exp(\beta F \eta / RT) - \exp[-(1 - \beta) F \eta / RT] \} \end{aligned} \quad (1.3)$$

where f , b represent forward and backward, respectively, and i_o , the so-called exchange-current density at $\eta = 0$, is given for concentration C_i & C_j of the reactants of the f & b steps, by:

$$\begin{aligned} i_o &= F k^{\circ}_f C_i (1 - \theta) \exp(\beta F \Delta \phi_r / RT) \\ &= F k^{\circ}_b C_j \theta \exp[-(1 - \beta) F \Delta \phi_r / RT] \end{aligned} \quad (1.3a)$$

Here the rate constants k° , represent the potential-independent

term in curly brackets in eqn. (1.1) and in particular, the chemical activation energy term $\Delta G^\ddagger$ in eqn. (1.2). These rate constants are for $\eta = 0$. At high values of the overpotential η , i.e. $\beta F\eta / RT \gg 1$, eqn. (1.3) becomes:

$$i = i_0 \exp (\beta F\eta / RT) \quad (1.4)$$

or

$$\eta = (RT/\beta F) \ln i - (RT/\beta F) \ln i_0 \quad (1.5)$$

This is a form of the well known Tafel equation $\eta = a - b \log i$, (writing $b = 2.3 RT/\beta F$) proposed by Tafel in 1905 on the basis of his experimental investigation of the h.e.r.¹⁰; b is the so-called Tafel slope.

1.3 Adsorbed intermediates in consecutive heterogeneous electrode processes

Electrode reactions are heterogeneous processes in which charge transfer occurs; their rates will therefore be influenced by (a) the adsorption and hence the surface concentration of the reactant ions at the interface; (b) the activation energy for the heterogeneous reaction at the surface, which will depend on the electrochemical nature of the reactants and the catalytic and adsorptive properties of the surface; (c) the presence of adsorbed intermediates and/or reaction products on the surface; and finally (d) the potential difference, $\Delta\phi$, at the interface (eqn. 1.2) which, amongst other factors, controls the rate of the charge-transfer reaction.

Factor (d) is the principal one that distinguishes electrochemical reactions from other heterogeneously catalyzed reactions

at the solid-solution interface; also, factor (d) strongly influences, and is closely related to, the factors a, b and c, for electrochemical reactions.

Electrode reactions are also influenced directly or indirectly by the specific surface properties of metals, e.g. the electronic work function, surface defect concentration, and the net adsorption energy for intermediates and reactants which may implicitly involve the energy for solvent molecule adsorption in situations where a solvent molecule must be displaced from the surface.

In fact, electrocatalysis is mainly concerned with the electrical behavior of intermediates which arise either in adsorptive and desorptive charge-transfer steps or with dissociative adsorption, e.g. as in the electrochemical oxidation of H_2 and organic molecules at Pt.

Historically, the evaluation of both the role and the adsorption behavior of intermediates has played a major part in the discussion of electrocatalysis and the mechanisms of electrode reactions of various kinds, in particular those leading to or from a gaseous substance, e.g. the h.e.r. and o.e.r. (oxygen evolution reaction), and the reverse processes of H_2 oxidation or O_2 reduction to water where a bond-dissociation step is required.

Most electrochemical reactions except perhaps one-electron ionic redox steps, proceed by at least two consecutive steps. In some cases, alternative desorption pathways in the overall

- 6 -

given reaction must also be considered, as in the h.e.r. and o.e.r.

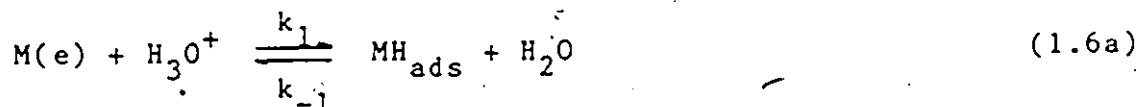
In consecutive reactions, it is always the step with the smallest rate constant (often referred to erroneously as the "slow" step; all steps in the steady-state have, of course, the same velocity) that is rate-determining. In alternative pathways, it is the path which proceeds with the greatest velocity that characterizes the kinetics of the overall reaction.

Since the electrochemical rates of various steps depend on potential, a step that is electrochemical rate-controlling at one potential may not necessarily be the kinetically limiting step at another potential. We shall encounter examples of this situation in the discussion of the experimental results for the h.e.r. to be given later in this thesis.

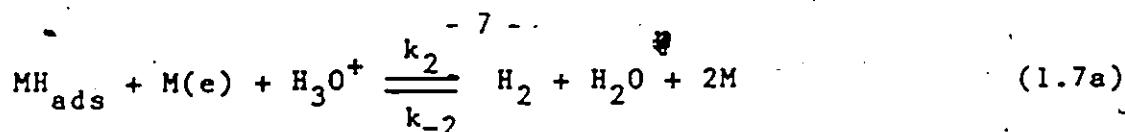
1.4 The h.e.r. as a model reaction of a multistep process

The h.e.r., which serves as a model reaction for electrode kinetic studies, has been most thoroughly and widely investigated. The likely reaction mechanisms which were revealed by early investigations¹⁰⁻²³ and are now commonly accepted²²⁻²⁷ are as follows:

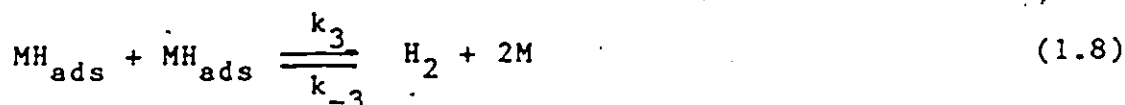
In acidic solution, the overall two-electron reaction involves first the discharge of a hydrated proton at the electrode surface with formation of an adsorbed H atom



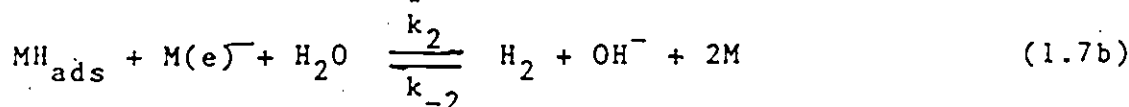
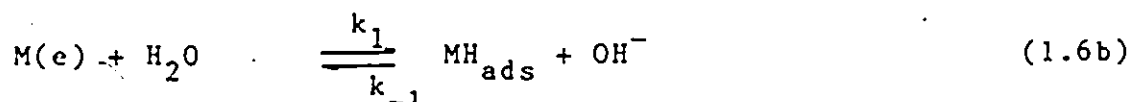
at some site on the metal electrode surface lattice. This must be followed by either an electrochemical-desorption step



or an heterogeneous chemical-recombination step



In alkaline solution, the mechanism is similar, except that the proton donor is a water molecule rather than H_3O^+ and the conjugate base product is OH^- instead of H_2O :



For the alkaline solution, the activation energy of the steps (1.6b) or (1.7b) will not generally be the same, respectively, as those for (1.6a) and (1.7a), so that the mechanism of the h.e.r. in acidic and alkaline solution at a given metal will not generally be the same.

Despite much work over many years, general agreement on the reaction mechanism, i.e. which step among the above reaction equations is respectively the rate-determining one at various metals, especially at the catalytically active ones, e.g. Pt, and in alkaline solution, has not yet been reached. Results depend much on the state of preparation of the surface of solid metals. Only for the h.e.r. at Hg as a liquid does a general consensus exist that step (1.6a) is rate-determining in acid²², 28-36.

1.5 Potential-dependence of coverage by adsorbed H

Extensive discussion of this problem has been given by Conway and Gileadi³⁷⁻⁴⁰. A general discussion, with the h.e.r. as

an example, is reviewed here.

1.5.1 Adsorption isotherms

Two general types of isotherms have been extensively employed in interfacial electrochemistry: the Langmuir and the Frumkin. The Langmuir adsorption isotherm is based on the assumption that the surface is homogeneous and that lateral-interaction effects are negligible. Implicit in both these assumptions is the presumption that the adsorbate randomly occupies sites on the adsorbent lattice.

In many systems of practical interest, a better approximation is obtained if it is assumed that the adsorption equilibrium constant K decreases exponentially with increasing coverage

$$\begin{aligned} K &= K_0 \exp (-\gamma\theta/RT) \\ &= K_0 \exp (-g\theta) \end{aligned} \quad (1.9)$$

An equivalent way of stating the same assumption is to say that the apparent standard free energy of adsorption varies linearly with coverage

$$\Delta G^\circ_\theta = \Delta G^\circ_{\theta=0} + \gamma\theta \quad (1.10)$$

This assumption gives rise to the Frumkin isotherm (see below) and can be shown to arise if pairwise interactions in the adlayer are taken into account, or if the surface is heterogeneous (p. 206)

The adsorption behavior of kinetically involved species in an electrode reaction may be examined in terms of either of two approaches: (a) the quasi-equilibrium hypothesis, in which it is supposed that all steps prior to the rate-determining one in the reaction sequence are almost in equilibrium, i.e.

the rate constant of the rate-controlling step is, say, at least ten times smaller than those of all other antecedent steps in both directions; or (b) the steady-state method, in which the rate of change of concentration of intermediates with time is equal to zero. The steady-state method is, in general, to be preferred but usually it leads to cumbersome expressions, so that numerical computing is usually required in order to obtain the predicted behavior.

For an electrochemical reaction involving adsorption of an intermediate in a discharge step (a so-called "electrosorption" reaction), the Gibbs energy of adsorption or electro-sorption, e.g. of H, differ from the chemical Gibbs energy of adsorption by an electrical free-energy term "VF". Thus, for a process such as step (1.6a) at quasi-equilibrium, the driving force for chemisorption of the H is potential-dependent so that the ratio of coverage, θ_H by H to free site availability, $1 - \theta_H$, follows a relation of the form

$$\theta_H / (1 - \theta_H) = K_c (C_H^+) \exp(VF/RT) \quad (1.11a)$$

This is a Nernst-type thermodynamic relation (in exp. form), analogous to the corresponding type of expression for the electrode potential of a redox reaction:

$$E = E_0 + RT/ZF \ln [OX]/[RED] \quad (1.12)$$

The Gibbs energy of electrosorption in eqn. (1.11a) is therefore of the form, $\Delta G_V = \Delta G_{V=0} + VF$, or more generally with eqn. (1.10), $\Delta G_V = \Delta G_{\theta=0, V=0} + VF + \gamma\theta$. Eqn. (1.11a) is fundamental for representing the potential-dependence of coverage by ad-species in u.p.d. processes. An analogous but more complex

expression arises for potential-dependence of steady-state coverage by an intermediate but then the relation has a kinetic rather than a thermodynamic significance (see eqns. (4.8) and (3.39) and refs. 25, 37-40).

1.5.2 Langmuir, quasi-equilibrium case

The Langmuir case for quasi-equilibrium conditions for the h.e.r. in acid solution will first be examined. As usual 23, 37-40, the primary discharge step is assumed to be almost in equilibrium, when either step (1.7) or (1.8) is rate-controlling; then θ_H can be written directly as eqn. (1.11a) (writing the overpotential η instead of the potential V in eqn. 1.11a), so that

$$\theta_H / (1 - \theta_H) = K^{\circ}_1 (C_{H^+}) \exp(\eta F / RT)$$

or

$$\theta_H = \frac{K^{\circ}_1 (C_{H^+}) \exp(\eta F / RT)}{1 + K^{\circ}_1 (C_{H^+}) \exp(\eta F / RT)} \quad (1.11)$$

where $K_1 = k_1 / k_{-1}$. Equation (1.11) is the electrochemical Langmuir adsorption isotherm modified to apply to the case of adsorption involving charge transfer as discussed above.

For convenience, in the above equations and all further material in this thesis, cathodic overpotentials associated with the forward direction of the h.e.r. will be taken with a positive sign, i.e. η is defined as $\Delta\phi_r - \Delta\phi$.

Since θ_H is generally a function of potential (see eqn. 1.11), so is the charge Q_f passed during the progress of the Faradaic electrosorption process; thus a type of differential

capacity may be defined as

$$C_p = dQ_f/d\eta = q_1 d\theta/d\eta \quad (1.13a)$$

where q_1 is the charge required to form a complete monolayer of the adsorbed species. C_p is termed the adsorption pseudocapacity. From eqns. (1.11) and (1.13a), C_p is found to be

$$C_p = q_1 F/RT \left[\frac{K^{\circ}_1 (C_{H^+}) \exp(F\eta/RT)}{[1 + K^{\circ}_1 (C_{H^+}) \exp(F\eta/RT)]^2} \right] \quad (1.13b)$$

A more complex equation results when g (eqn. 1.9) is not zero; then the potential-dependence of C_p differs from that given by eqn. (1.13).

1.5.3 Frumkin isotherm; quasi-equilibrium case

With the assumption that the primary discharge step (eqn. 1.6) is almost in equilibrium and applying eqn (1.9), we find (cf. refs. 23, 37-40).

$$\theta_H/(1-\theta_H) \exp(g\theta) = K^{\circ}_1 (C_{H^+}) \exp(\eta F/RT) \quad (1.14)$$

the Frumkin isotherm, from which the Langmuir isotherm follows as a special case when $g=0$.

At intermediate values of the coverage ($0.2 < \theta < 0.8$) and for sufficiently large g , the exponential term in eqn. (1.14) predominates and upon taking logarithms of both sides and neglecting the term $\ln(\theta/(1-\theta))$ one obtains

$$\theta_H = 1/g (\ln K^{\circ}_1 C_{H^+}) + F\eta/gRT \quad (1.15)$$

This relation has the form of the Temkin isotherm but his derivation and assumption (heterogeneous surface) were different from those implied here (interaction effect). The Temkin beha-

behavior is characterized by a linear dependence of coverage on the potential and a logarithmic dependence on the concentration, C_H here.

When the Frumkin isotherm (eqn. 1.14) applies, θ_H cannot be written as an explicit function of η and so C_ϕ can be expressed only as a function of θ_H

$$C_\phi = q_1 F/RT \left[\frac{\theta_H(1-\theta)}{1 + g\theta_H(1-\theta)} \right] \quad (1.16)$$

which can, of course, be numerically evaluated as a function of η by means of a computer (see refs. 37-40), using eqn. (1.14).

1.5.4 Steady-state approach

The expressions given above for the adsorption isotherm and the pseudocapacitance of an electro-active chemisorbed species pertain to equilibrium or near equilibrium situations, e.g. as in u.p.d. or for steps prior to a clearly rate-determining process in a consecutive reaction sequence, e.g. in the h.e.r.. It should be mentioned here, that more generally, a steady-state condition for the kinetics of a consecutive step reaction can be set up which leads to corresponding steady-state coverage vs potential relations. These can be evaluated numerically and form the basis for a kinetic theory of a.c. impedance and potential decay behavior which will be discussed in chapter 4.

The steady-state treatment of these quantities is a more realistic approach to the adsorption behavior of o.p.d. species since under o.p.d. condition net, and often appreciable, Faradaic

currents for the overall reaction are passing.

1.5.5 O.p.d. H coverage

The coverage θ_H of the reaction intermediates can be evaluated as a function of overpotential by integration of the C_ϕ vs η profile (i.e. the peak area of C_ϕ vs η curves):

$$q_1 \int_{\theta_{H,0}}^{\theta_H} d\theta_H = \int_0^\eta C_\phi(\eta) d\eta$$

Thus

$$\theta_H = 1/q_1 \int_0^\eta C_\phi d\eta + \theta_{H,0} \quad (1.17)$$

where $\theta_{H,0}$ is the coverage at $\eta=0$, i.e. the condition of equilibrium. Since only the cathodically adsorbed and kinetically involved H is of interest, the $\theta_{H,0}$ can, in some cases be assumed to be equal zero for most cases of o.p.d. measurements. At Pt, of course, full coverage of H already exists as u.p.d. H at $\eta=0$ ^{23,76} so the o.p.d. H is in excess of this coverage.

Surprisingly the pseudocapacitance behavior of o.p.d. species has hitherto received very little attention experimentally but rather only in terms of theoretical treatments³⁷⁻⁴⁰. This situation has arisen because, hitherto, no satisfactory means of experimental measurement has existed for obtaining the required information for o.p.d. species, while, by contrast, much knowledge exists on u.p.d. species^{1,23,41,42,76}.

Therefore, it is the purpose of the thesis to describe development of new methods for experimental study of the pseudocapacitance behavior of o.p.d. species, especially H in the

h.e.r., and analyze the significance of such results.

1.6 H adsorption and electrocatalysis in the h.e.r.

Electrochemical polarization performance is characterized by two fundamental parameters: (a) the exchange current density, i_0 , and (b) the slope of the relation between $\log(\text{current-density})$ and potential, called the Tafel slope b . Ideally, a combination of high i_0 and low b values is the condition required for optimizing cathode performance but this not always is feasible, i_0 and b values for a given process being normally not independent quantities.

Generally speaking, the desirability of a low slope b parameter, has not been fully appreciated -- it is a principal factor allowing low polarization to be maintained up to relatively high current-densities and a low rate of change of η for a further increase of current-density. Most characterizations, 26,43,44,50,52 of electrocatalysis at various metals have been concerned with the value of the exchange current density, i_0 . Optimization of performance through the latter parameter is achieved by using certain favorable metals and, in particular, large specific-area materials, that is porous-type electrodes that can provide low real current-densities based on a large real area of the electrode.

Both i_0 and b for the h.e.r. are closely related to the adsorption behavior of the H atom reaction intermediate on the electrode surface: the former (i_0) on the standard Gibbs energy of adsorption of $H^{24,44}$ and the latter (b) on the potential dependence of the coverage by H.

1.6.1 Exchange current density i_0 and electrocatalysis

Electrode reactions may be broadly divided into two types: (a) those in which chemisorption of reactants, intermediates or products play a role in the kinetics and mechanism of the processes and (b) those in which the electrode acts simply as a source or sink of electrons. It is in the case of the first class of reactions that electrocatalysis is normally manifested on account of formation of chemisorption bonds and change of the surface structure of the electrodes.

1.6.1.1 Relations of i_0 , ϕ and $\Delta H_0^\ddagger$ in the simplest case

A convenient reaction of the second type, referred to above, is



such as has been subjected to a detailed examination e.g. by Bockris, et al.⁴⁵. They found that the heat of activation, $\Delta H_0^\ddagger$, for reaction (1.18) at various cathode materials was essentially independent of the electron work function, ϕ , of the metal. However, a linear relation between the electron work function and i_0 values was obtained for the various metals investigated. From the absence of a dependence of $\Delta H_0^\ddagger$ on the ϕ , strong evidence for an electron-transfer, non-bonding mechanism, i.e. not involving chemisorption, for redox reactions with species involving aquo-ligands was thus obtained⁴⁶⁻⁴⁹. The variation in i_0 of the reaction with the nature of the substrate was said to be due to secondary effects on the reactant concentration caused by the double-layer structure; however, this itself must be due to some adsorption influence from the electrode metal, e.g. differences in the solvent adsorption behavior.

1.6.1.2 Variation of i_0 with ϕ , ΔH_{ads} and MH interaction in the h.e.r

The effect of the substrate on the rate of reactions when one or more reactants or products are adsorbed on the electrode is much more pronounced than in the simple case discussed above. Here, the substrate affects the heat of activation and, because i_0 is related exponentially to the heat of activation (see eqn. 1.3a), the i_0 value can vary over many orders of magnitude on account of different values of the heat of adsorption of one of the reactants or products. The strength of adsorption bonds will affect both the surface concentration term for the intermediate and the Gibbs energy of activation in the rate equation²⁴. An analysis of these effects for the h.e.r. was given by Parsons⁴⁴ and by Gerischer⁴⁸.

Kita⁵⁰ has correlated i_0 for the h.e.r. in acid solution with the heat of adsorption of H for a number of d- and sp-metals (see Fig. 1.1). From Fig. 1.1, it can be seen that the behavior of d-metals is distinctly different from that of sp-metals, namely the activity of d-metals has a tendency to decrease with increase of $-\Delta H_{ads}$, whereas the activity of sp-metal remains almost unchanged. The d-orbital metals exhibit a periodic dependence of the i_0 on their atomic number (see Fig. 1.2), with highest exchange current densities corresponding to Ni, Pd, and Pt in the three transition metal series. The heat of adsorption is correlated reasonably well with the atomic number and the column in the periodic table. A similar periodicity for the hydrogen electrode reaction was first suggested by Bockris⁵¹ and the $\log i_0$ vs ΔH_{ads} relation was first

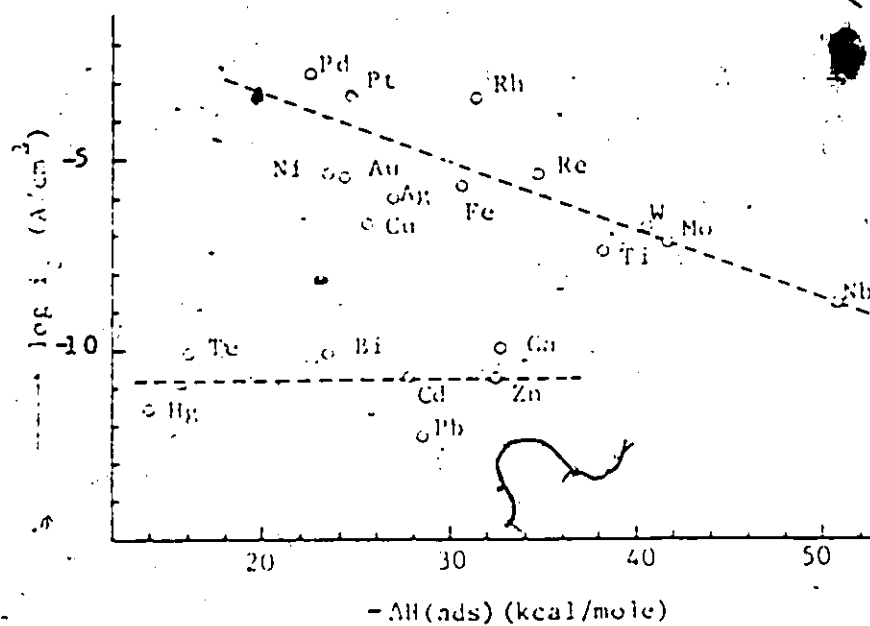


Fig.1.1 Correlation of log exchange current with heats of adsorption of H_2 . (Fitts, 1966)

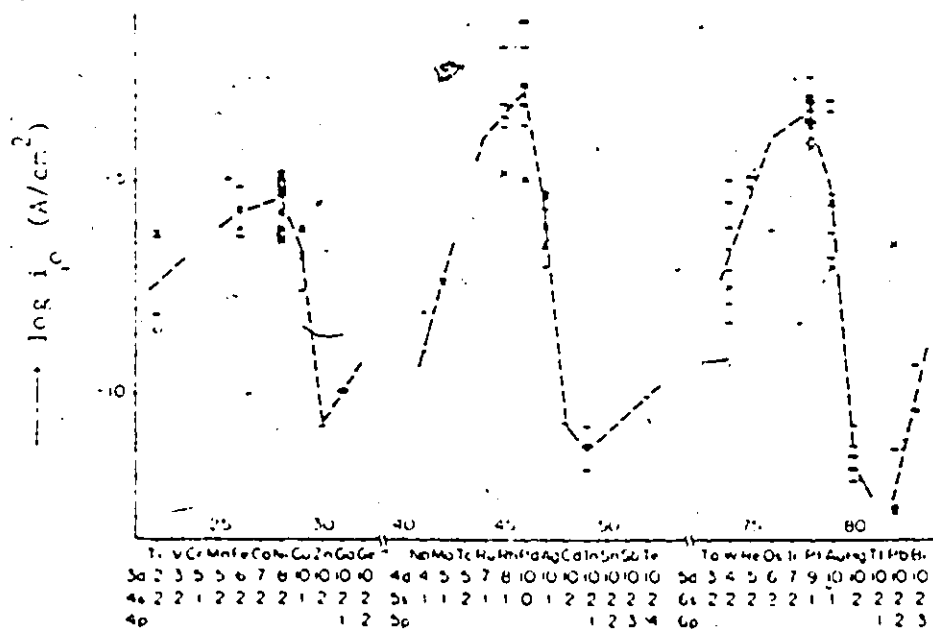


Fig.1.2 Periodicity of exchange current density for H_2 generation on metals (Kita, 1966). $\bullet$ acid solution, $\times$ alkaline, $\circ$ neutral.

given by Conway and Bockris⁵² and later treated by Parsons⁴⁴.

A corresponding relation of $\log i_0$ to ϕ (see Fig. 1.3) can be demonstrated⁵³; in fact two straight lines with opposite slopes represent the behavior of high overpotential metals on the one hand and the medium or low-overpotential metals on the other (see Fig. 1.3). These relations are consistent with the view that the "slow" discharge mechanism is operative at the high-overpotential metals and that the electrochemical desorption step controls the rate in the case of the medium-overpotential metals^{24,26}. Probably H atom recombination control determines the kinetic behavior at the lowest overpotential metals, e.g. active Pt, Rh, Ir and Pd.

Conway and Bockris pointed out⁵² that the electron work function increases with percentage d-character in the dsp hybrid bonding in transition metals. Thus, since there is a linear relationship between the work function and $\log i_0$, a similar relationship between percentage d-character and $\log i_0$ should be expected for the transition metals and this was found by Conway and Bockris⁵².

The greater the percentage d-band character, the smaller is the number of unpaired electrons in the d-band. The lesser the number of unpaired electrons, the lower should be the heat of adsorption of hydrogen on the metals, for there will be a diminished tendency for electrons in the metals to pair with the 1s electron of the hydrogen atom. This prediction is confirmed by plotting the experimental (initial) heats of adsorption of hydrogen on metals versus the percentage d-band

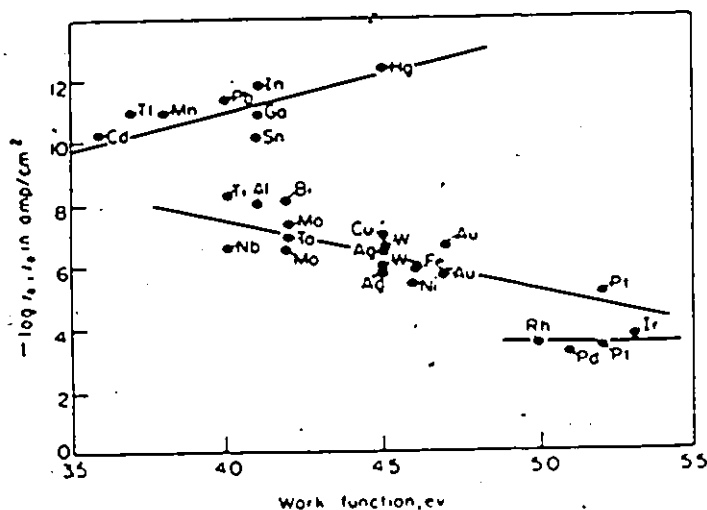


Fig. 1.3 Relationships of $\log i_0$ vs work function for hydrogen evolution on the high-overpotential, medium-overpotential and low overpotential metals⁵³.

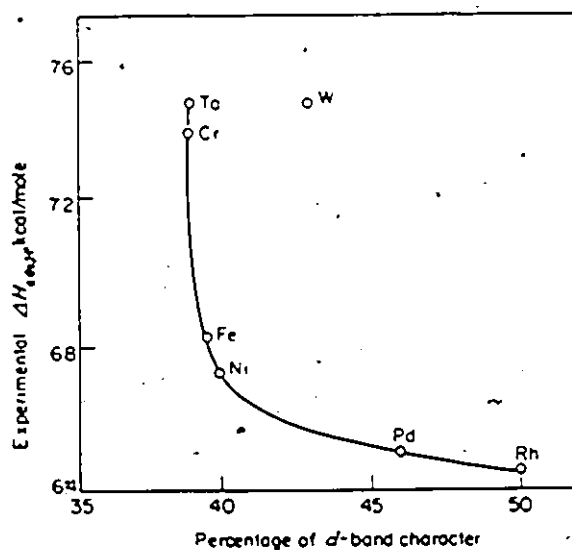


Fig. 1.4 Plot of heat of adsorption of hydrogen on the metal ($\Delta H_{ads,H}$) versus percentage d-band character for several metals⁵².

character⁵² (see Fig. 1.4).

A plot was also made of the overpotentials at a constant current density of 10^{-3} A cm⁻² versus the MH bond energy for a number of metals⁵² (see Fig. 1.5). For this purpose, the bond energy D_{M-H} was calculated using Pauling's equation⁵⁴ as suggested by Eley⁵⁵:

$$D_{M-H} = \frac{1}{2}(D_{M-M} + D_{H-H}) + 23.06 (X_M - X_H)^2 \quad (1.19)$$

where D_{M-H} and D_{H-H} are the bond dissociation energies of two adjacent metal atoms on the surface of a metal and of molecular hydrogen, respectively. X_M and X_H are the electronegativities in electron volts of the metal and H atoms, respectively.

Ruetschi and Delahay⁵⁶ made the first plots of $\log i_0$ as a function of D_{M-H} by an equation related to (1.19) by neglecting the rather important electronegativity term. Because of this omission, their results differed in direction and significance from those of Conway and Bockris⁵² who utilized the complete eqn. (1.19) to calculate D_{M-H} , which gave a better rationalization of the $\log i_0$ vs D_{M-H} behavior.

In the η vs D_{M-H} plots, two distinct groups of metals are indicated (see Fig. 1.5). In one group, which consists of the transition metals, η increases as D_{M-H} increases. On the other hand, for the group of metals Hg, Pb, and Tl, η decreases with increasing D_{M-H} . In the "slow"-discharge mechanism of the h.e.r. (step 1.6), the rate-determining process involves electrosorption of atomic H on the metal (see eqns. 1.6-8). Thus, an increase in the heat of adsorption of hydrogen on the metal should accelerate the reaction. Conversely, in the "slow"-electrochemical

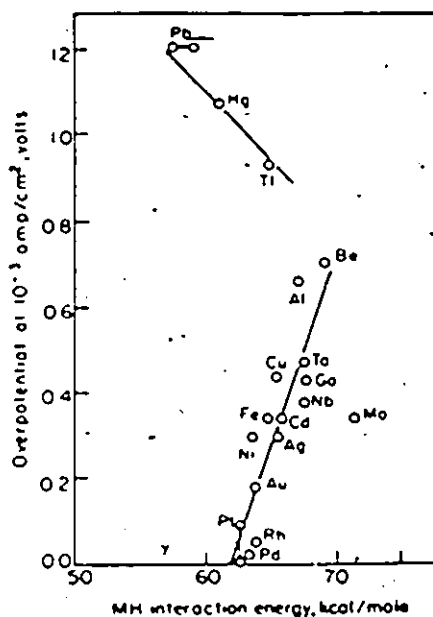


Fig. 1.5 Plot of hydrogen overpotential at a constant current density versus heat of adsorption of hydrogen for several metals⁵²

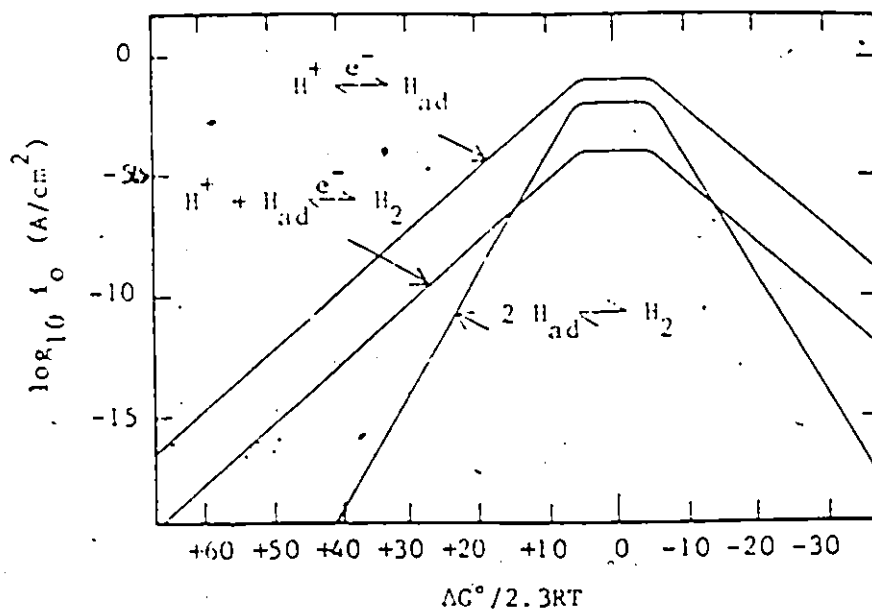


Fig. 1.6 Volcano curves for reactions 1.6, 1.7 and 1.8, Logarithm of exchange current densities versus standard Gibbs energies of adsorption for H ($B=0.5$)⁴⁴

desorption mechanism of the h.e.r., an hydrogen atom is desorbed from the surface in the rate-determining step. Hence, a decrease in the heat of adsorption should accelerate the reaction. These results, along with other evidence²²⁻²⁷, confirm the view that a rate-determining discharge mechanism applies at Hg, Pb, and Tl, while a rate-determining electrochemical desorption and/or chemical-recombination desorption step obtains at most of the transition metals.

Parsons showed⁴⁴ that i_0 for each of the various component steps (one of the reaction eqns. 1.6, 1.7 and 1.8 is the r.d.s.) is expected to be correlated with the Gibbs energy of adsorption (ΔG°) of H_2 ($\frac{1}{2}H_2 + M = MH$) on the surface. Such correlations are represented by volcano curves of the type shown in Fig. 1.6 when β for each of these reactions is $\frac{1}{2}$, i.e. the Gibbs energy barriers are all symmetrical. The flat region at the top of each curve corresponds to a Temkin region of the adsorption isotherm, if it arises. In fact, Bockris and Conway's results^{52,57,58} are consistent with the existence of two different mechanisms, both of which give volcano expressions with a maximum rate when ΔG° for the r.d.s. is zero. However, only the ascending branch (ΔG° positive, $\theta \ll \frac{1}{2}$) of one mechanism, the discharge r.d.s., is experimentally accessible. Similarly, only the descending branch (ΔG° negative, $\theta \gg \frac{1}{2}$) for the other mechanism, electrochemical-desorption r.d.s., is observed experimentally. For metals that have ΔG° close to zero, a third possible volcano expression can arise when the recombination reaction is the r.d.s.

It is interesting that in Parsons' derivation of the volcano relations for $\log i_0$ as $f(\Delta G_H^\circ)$ in the h.e.r., it is shown that the principal effect of changes of ΔG_H° arises from their influence on the coverage θ_H rather than on the energy of activation which enters the result as the sum of $\Delta G^\ddagger$ values for the forward and backward steps of the reaction involved and this sum is approximately independent of ΔG° .

1.6.2 Tafel slope b and electrocatalysis

One essential difference between electrocatalytic and catalytic processes is that the velocity of an electrocatalytic step when it involves charge-transfer depends exponentially upon the overpotential η (see eqns. 1.3-4). Thus, the energy of activation for the electrocatalytic, really an electrosorption reaction, is linearly reduced by the overpotential (see eqn. 1.2).

The dependence of $\log(\text{current})$ upon η is characterized by the Tafel slope $b = d\eta/d\log i$. The relationship between b and the potential-dependence of the coverage of the adsorbed intermediate can be shown by means of the following equations. From eqns. (1.1) and (1.2), the rate equation for an electrochemical process involving adsorption of the intermediate can be written as

$$i = nFk^\circ(C_R)_s\theta_H(\eta)\exp(\beta F\eta/RT) \quad (1.20)$$

where k° is the rate constant including all the potential-independent constants in eqns. (1.1) and (1.2); $\theta(\eta)$ is a general function for dependence of coverage θ in η which is $(1-\theta_H)$ for a r.d.-discharge process and θ_H for a r.d.-electrochemical

desorption process.

The reciprocal of the Tafel slope can be expressed by:

$$1/b = d \log i/d\eta = d \log \theta(\eta)/d\eta + \beta F/2.3RT \quad (1.21)$$

adsorption
factor

charge-transfer
factor

The Tafel slope b thus is seen to depend both on the adsorption factor for the behavior of atomic hydrogen in the h.e.r., and on the charge-transfer factor.

The charge-transfer factor arises in all electrode processes due to the modification of Gibbs energy of activation of the process by the electrode potential, analogous to the Brønsted linear free energy relation⁵⁹, referred to earlier, as exemplified by eqn. (1.2). The adsorption factor which is related to the differential coefficient of the adsorption factor $\theta = f(\eta)$ (e.g. see eqn. 1.11), with respect to η is thus related to the adsorption pseudocapacitance (see eqns. 1.12 and 13).

An important result of eqn. (1.21) is that the larger is the value of the adsorption factor in eqn. (1.21), the lower and thus more favorable, is the value of b . In the discussion which will follow, it will be shown that the adsorption term in eqn. (1.21), hitherto rather neglected as a factor in electroanalysis, is very important in determining favorable electrocatalytic behavior of active electrodes for high current density operation.

The Tafel slope b has certainly been an intensively studied experimental parameter especially in relation to reaction

mechanism, e.g. in various works of Bockris^{24,26,60,64,65}, Parsons^{29,66-68}, Conway⁶⁹⁻⁷¹ and Despic^{72,73}.

In the case of the h.e.r. at Hg²⁸⁻³⁶, the experimentally observed b value of 0.118 V can be explained with eqn. (1.21) assuming the discharge reaction is the r.d.s. and is associated with $d \log \theta_H / d\eta = 0$, $1 - \theta_H = 1$, and taking $\beta = 0.5$ and $T = 298K$. For the h.e.r. at Pt, with an observed b value of ca. 0.030 V^{60-63,80} at low current-densities, the behavior can be accounted for in terms of recombination of the o.p.d. chemisorbed H as the r.d.s. Thus with the rate equation

$$i = 2Fk_3\theta_H^2 \quad (1.22)$$

and applying eqn. (1.11) by the widely-accepted treatment^{24,26,80} for the condition $\theta_H \rightarrow 0$ as $\eta \rightarrow 0$ the resulting value for b would be 0.029 V at 298 K. However, the assumption $\theta_H \rightarrow 0$ is certainly incorrect, since we know^{74,100} from reliable u.p.d. experiments that the coverage of H at Pt electrode should be high and already near unity at $\eta = 0$. In the present thesis, special consideration will be given to this problem in relation to the experimental determination of o.p.d. coverage at Pt and other metals.

From eqn. (1.21), it is clear that the analysis of the Tafel slopes can be ambiguous without experimental information about the adsorption behavior of H. This can be illustrated by reference to the following examples.

In the case of the h.e.r. with discharge followed by rate-determining electrochemical desorption (eqn. 1.7), if $\theta_H(V)$ can be represented by eqn. (1.11) and assuming $\theta_H \rightarrow 0$, or $K_1(C_{H^+}) \exp(\eta F/RT) \ll 1$, as discussed by Bockris²⁴, then eqn.

(1.21) gives $1/b = (1+\beta) F/2.3RT$ or $b = 0.039$ V at $\beta = 0.5$, $T = 298$ K. However, if θ_H is constant with η , eqn. (1.21) gives $1/b = \beta F/2.3RT$ or $b = 0.118$ V with the same β and T as above. The latter situation arises in the results presented later in this thesis for the case of the h.e.r. at Ni and unactivated Pt.

Another example is when the experimentally observed value of $b = 0.118$ V can be explained either in terms of the discharge step (eqn. 1.6) being as rate-determining with $\theta_H \rightarrow 0$ or by the electrochemical-desorption step being rate-determining (eqn. 1.7) with $\theta_H \neq f(V)$. However, in the latter case, the coverage of H should be significantly or especially greater than 0, if the rate constant of the adsorption step (k_1) is much greater than that of the desorption step (k_2). Therefore, the determination of θ_H is an important criterion for determining whether the discharge or electrochemical-desorption step is rate determining when a Tafel slope of ca. 118 mV is observed at 298 K.

1.7 Problems related to the experimental study of the h.e.r.

There are two major problems with regard to the state of experimental knowledge concerning the behavior of the h.e.r., e.g., at Pt and especially at base metal cathode materials, e.g. Ni; a) the coverage of the cathodically adsorbed, kinetically involved H species (the o.p.d. H) has hitherto not been reliably measured as a function of potential (see below) or even evaluated at all; b) the electrocatalytic activity of Pt electrodes is poorly reproducible and depends sensitively on solution and surface preparation, and on cleanliness, and the relation of its activity to o.p.d. H coverage has remained largely

undetermined.

The first difficulty is that virtually all of our present knowledge about the adsorption behavior of H atoms on active metal electrodes as a function of potential has been derived experimentally at noble metals, especially Pt, by means of charging curve^{22,23,74,75}, a.c. impedance^{22,23,76,77} or cyclic-voltammetry (CV) methods^{78,79}, and refers only to the strongly bonded, so-called "underpotential deposited" u.p.d. adatoms, at the electrode surface, which are not necessarily^{80,81} those involved kinetically in the steady-state of the h.e.r. at appreciable Faradaic current-densities (for more details, see section 1.8). By contrast, virtually nothing is known about the coverage of the o.p.d. H as a function of cathodic overpotential except that, in theoretical discussions of the mechanism of the h.e.r. at Pt, a small but exponentially potential-dependent coverage, θ_H , by o.p.d. H species has been suggested^{80,81} in order to account for the observed "recombination Tafel slope" of ca. 30 mV at active Pt electrodes. However, these are otherwise known⁴¹ to be fully covered already at the reversible potential by u.p.d. H, so that at cathodic overpotentials some further increase of this coverage beyond $\theta_H = 1$ would be expected. However, an alternative mechanism was proposed by Breiter⁷⁷ to account for this slope at highly active electrodes and involves diffusion of molecular H_2 from the electrode, resulting from a supposed local supersaturation of H_2 near the cathode surface and an influence of the back-reaction of H_2 dissociation on H coverage.

The second difficulty is as follows: it is well known^{23,27,}

77,82-89 that the electrochemical behavior of the Pt electrode depends to a great extent on its pretreatment, the state of its surface and the presence or absence of chemisorbed impurities, perhaps much more so than at most other metals except platinum's own congeners in group VIII. Thus, it has been recognized⁸²⁻⁸³ that even trace impurities at the level of 10^{-10} mol dm⁻³ can significantly poison the electrode reaction. A variety of discrepant experimental observations has been reported for Pt in the literature, so that the mechanism of the h.e.r. at Pt and especially the behavior of the o.p.d. H are still controversial subjects but ones which are of major interest in understanding the behavior of Pt in relation to its importance in the field of electrocatalysis, e.g. in fuel-cell and electrolyser development^{90,91}, and fundamentally as a prototype example of a catalytic and strongly adsorptive surface, in contrast to Hg.

Another important gap in knowledge of the behavior of H atom adsorption in the h.e.r. exists for the base metals, e.g. Ni or Fe which are practically important electrolyser cathode materials. In these cases, study of u.p.d. H behavior (if it arises) cannot be carried out because of onset of surface oxidation at these metals either near or already at the H₂ reversible potential in alkaline solution, or of dissolution of the metals in acidic solution. At cathodic overpotentials, no satisfactory experiments have been performed to examine the coverage and state of the o.p.d. H; only some involvement of diffusion of H into these two metals has been investigated in relation to

hydride formation and metal embrittlement by sorbed H.

In the work to be described in the present thesis, it has been shown, for the first time, how the electrochemical adsorption behavior of the kinetically involved, adsorbed o.p.d. H intermediates in the h.e.r. at Ni, Ni-Mo-Cd plated alloys, Au and Pt electrodes in acid and alkaline solution can be determined by means of: a) the new procedure employing open-circuit potential decay measurements⁹²⁻⁹⁵ and b) a.c. impedance measurements, interpreted with aid of a newly developed treatment⁹⁶⁻⁹⁸, applied to the behavior of the h.e.r. at Ni, Ni-Mo and Pt electrodes.

In order to deal in satisfactory way with the state of Pt electrode surfaces and their cleanliness, a point-by-point anodic activation procedure was employed which gave excellent reproducibility. Based on the "clean surface" behavior thus observed, the effects of impurities on the o.p.d. H adsorption behavior could then, for the first time²⁷, be studied. In a sense, the mechanism of the h.e.r. at Pt in the presence of trace impurities is practically of more importance than in the absence of impurities, if we think only that the most active electrocatalytic systems in engineering applications^{90,91} usually have to tolerate, and be operated with, significant levels of impurities in the electrolyte or gas streams. Nevertheless, knowledge of the fundamental behavior of the Pt electrode under the cleanest conditions possible is essential in order to provide a basis of reference for proper understanding of the kinetics of the h.e.r. at this important metal.

1.8 U.p.d. H and its relation to o.p.d. H

The phenomenon of so-called 'underpotential deposition' (u.p.d.) of strongly bound adatoms at electrode surfaces has been widely studied and well characterized both experimentally⁹⁹⁻¹⁰³ and theoretically^{37-40,104,105}. Such species arise by Faradaic deposition, usually in submonolayer arrays, at potentials corresponding to lower energies than those for deposition of the same element in the bulk state at unit activity, i.e., in the case of H, at potentials below the reversible potential for the h.e.r.

In most cases, it is believed^{80,100-106} that these strongly bound u.p.d. species are not necessarily the kinetically involved intermediates in the corresponding overall continuous Faradaic reaction, e.g. for H_2 , Cl_2 , O_2 evolution and bulk metal electrocrystallization processes. This is certainly the case for u.p.d. H in the h.e.r. at Pt where θ_H is already near 1 at the reversible potential ($\eta=0$).

Experimentally, u.p.d. is easy to study since the small current densities associated with deposition or desorption of monolayer arrays 'by definition' suffer, unlike determination of o.p.d. H, no interference from any large currents of parallel Faradaic processes associated with the corresponding bulk reaction.

In order to understand the kinetics of multistep Faradaic reactions of the electrocatalytic type, e.g. the cathodic h.e.r., it is necessary^{68,107} to have information on the adsorption behavior of the 'overpotential deposited' (o.p.d.) interme-

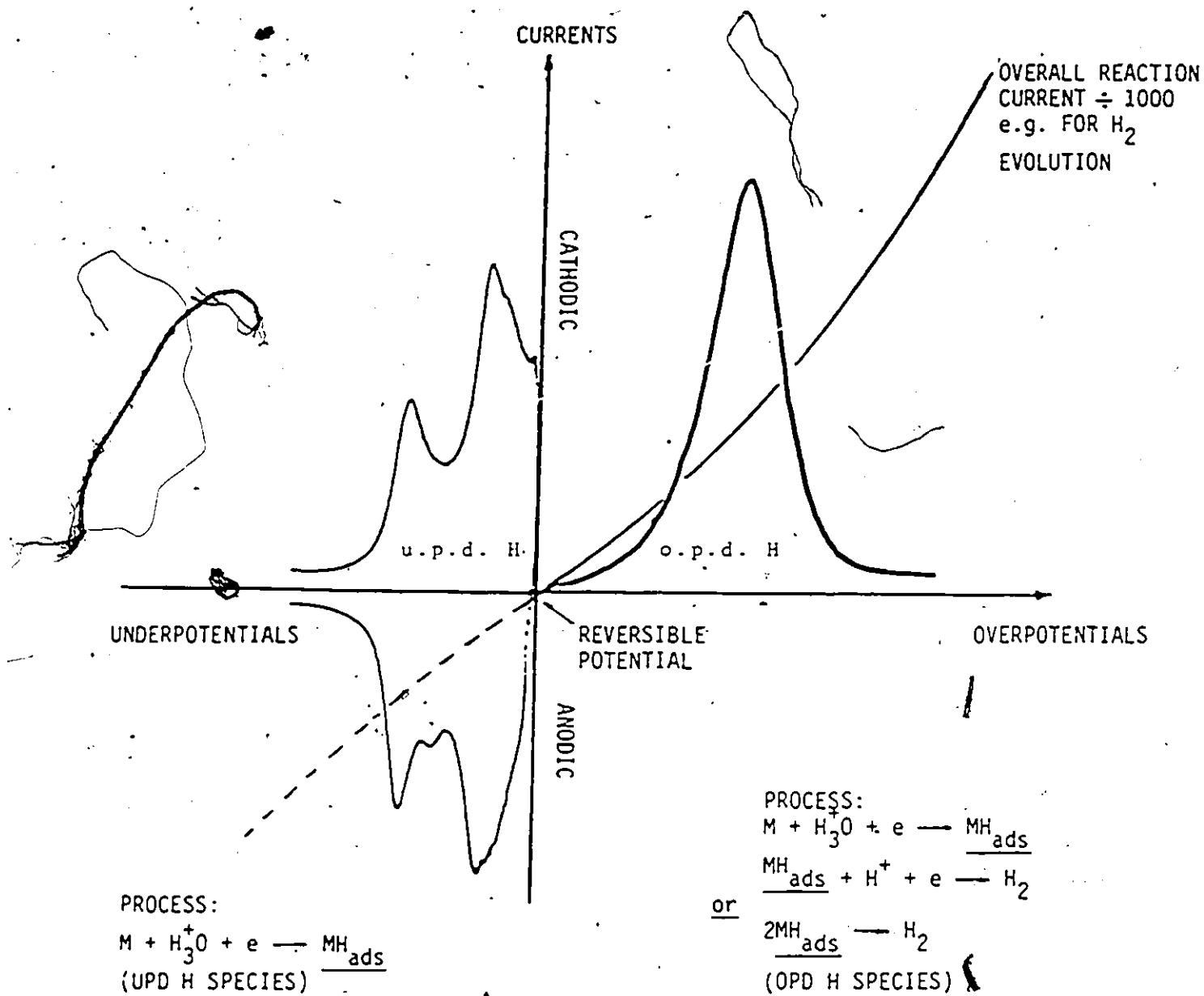


Fig. 1.7 Schematic representations of the u.p.d. H and the o.p.d. H in faradaic reactions.

species that are deposited (and removed) in the steady-state of the Faradaic reaction proceeding at appreciable net current densities, i . In fact, the coverage terms involved in the kinetic rate eqn. (1.11) must refer to the o.p.d. H. Up to the present, it is surprising that there are no reliable experimental data for the behavior of o.p.d. H recorded in the literature; this is because of the difficulties associated with application of hitherto existing experimental techniques (see the following section).

This situation can be illustrated in Fig. 1.7, for the u.p.d. and o.p.d. H CV profile at Pt electrode. "Under" the reversible potential for H^+/H_2 ($E=0$), there is no net Faradaic reaction (i.e., hydrogen oxidation reaction) current passing at the Pt electrode surface, because N_2 is normally continuously bubbled through the solution, so that no H_2 exists in the solution. Formation of u.p.d. H, associated with very small currents, can be easily detected as two or three peaks in the current vs. potential plot of a cyclic-voltammogram (see Fig. 1.7) which correspond to different adsorption states. However, if the potential is "over" the reversible potential, a large Faradaic current, due to the h.e.r., which is at least 10^3 times higher than the u.p.d. currents, makes measurement of currents for the o.p.d. H on the electrode surface impossible to observe by the CV method (a current component would exist for changing o.p.d. H coverage with change of η - see below, chapter 4).

It is of interest that u.p.d. of ad-species in electrochemical reactions rarely follows equations (1.15), (1.14) or (1.11). More commonly, a multiplicity of discrete adsorption

states can be resolved below monolayer coverage over an appreciable potential (electrochemical Gibbs energy) range of ca. 0.3 - 0.6 V, even at well defined single-crystal surfaces. However, the discrete states that can often be experimentally well resolved by electrochemical methods, e.g. cyclic-voltammetry (see Fig. 1.7 as an example) are each quite well represented by the Langmuir isotherm (eqn. (1.11)) and each has a characteristic K_1 value or standard chemical free energy of adsorption⁴¹. This discrete adsorption behavior does not necessarily apply to o.p.d. species, as will be shown later.

1.9 Problems with some previous approaches for o.p.d. H determination

Methods for study of the adsorption of intermediates have been discussed in references 25, 37, 108. The most generally applicable methods are based on observation of the electrical effects associated with causing changes in the extent of coverage of the electrode by the Faradaically deposited* electroactive intermediates. This can be achieved by "charging" or "discharging" the surface layer either galvanostatically or potentiostatically.

1.9.1 Charging curve and cyclic-voltammetry methods

There are two common procedures used widely in the study of the adsorption behavior: a) the galvanostatic charging method,

* In certain cases, e.g. in H_2 oxidation, the reverse of the h.e.r., the H intermediate may arise by a dissociative chemisorption step, $H_2 + 2M \longrightarrow 2MH_{ads}$, followed by electrochemical oxidation of the adsorbed H (reverse of step 1.6).

which originated in studies of the capacity of the double-layer at Hg by Bowden and Rideal¹⁰⁹ and was extended by Frumkin and co-workers^{15,16,75} particularly to studies of H desorption by various other workers^{74,110-112}; b) the cyclic-voltammetry (CV) method^{100,113-116}.

These two techniques have high sensitivity and accuracy for determination of coverage and pseudocapacitance behavior of u.p.d. species. Especially suitable is the cyclic-voltammetry method for resolution of multiple states of adsorption in u.p.d. which gives directly information in C_p . These methods are, however, inapplicable or applicable only with difficulty over potential ranges where the Tafel relation for appreciable continuous currents applies, giving potential-dependent background currents for the main Faradaic reactions that are orders of magnitude larger than those corresponding to changes of coverage by the chemisorbed intermediate species, as illustrated in Fig. 1.7 and discussed in the last section.

At active Pt electrodes, for example, difficulties are encountered in using the anodic charging curve method^{74,77} with transients taken from cathodic overpotentials, especially when high cathodic currents have been previously passing, owing to reoxidation of readsorbed dissociated H_2 , as was found and discussed by Breiter et al.^{74,78}. Thus, these authors were able to evaluate total H charges for several H_2 evolution cathodic current-densities that were previously passing and as a function of anodic stripping current densities. However, the results demonstrated that H, dissociated and readsorbed from H_2 , made a

contribution to the total H oxidation charge measured when H_2 bubbles had been generated by previously passing cathodic current when the latter was large. Also, more generally, anodic transients taken from cathodic overpotentials include charge contributions from both o.p.d. and u.p.d. H which are not always easy to separate.

In a different approach, but also using anodic charging curves, attempts were made by Bockris et al.¹¹⁰ and by Devanathan and Selvaratnam¹¹¹ to measure o.p.d. H at Ag and Ni by means of a "double charging" method. However, the results obtained cannot be considered satisfactory owing to the large metal "surface oxidation" corrections that are required in this procedure; an uncertainty of 25% was stated in ref. 110.

1.9.2 A.c. impedance method

Another powerful procedure for u.p.d. and o.p.d. adsorption measurements is the a.c. impedance method^{86-89,117-130}. Although this technique has been used to study the u.p.d. H, for example, on Pt electrodes^{23,76,77}, there are surprisingly few impedance studies on the h.e.r. in the overpotential region.

Gerischer and Mehl¹¹⁷ made impedance studies of the h.e.r. at mercury, silver and copper electrodes at appreciable overpotentials. The treatment presented there is applicable only sufficiently far from the reversible potential that the Tafel approximation holds. This restriction means that the important potential region, especially at Pt, over which the surface coverage is changing appreciably with potential was eliminated from the measurement. Furthermore, their theory did not fit the expe-

rimental data well, and the observed frequency dispersion was ascribed to spurious effects^{117,123} but probably was actually a fundamental aspect of the behavior of the adsorbed H (see section 3.2).

In Breiter's a.c. impedance work^{76,77}, the adsorption pseudocapacitance of u.p.d. H at Pt was evaluated at various frequencies as a function of anodic potential; the behavior was in good agreement with that derived by means of anodic charging curves⁷⁴ and with other cyclic-voltammetry results. The impedance behavior was also evaluated at small cathodic overpotentials at active Pt electrodes and indicated, surprisingly, a role of diffusion of molecular H_2 from the electrode in the kinetic behavior, as was mentioned in section 1.7. However, the results in the o.p.d. potential regions were not related to the adsorption behavior of H as a function of cathodic overpotential, that aspect being obscured apparently by the H_2 diffusion effect.

Armstrong and Bell¹³¹ made a useful a.c. impedance study of the h.e.r. on rotating W and WC electrodes at potentiostatically-controlled overpotentials. The observed impedance spectra, plotted in the complex-plane, were single distorted semi-circles. The u.p.d. of the electrodes was reported and a supposed double-layer capacitance (see Errata in ref. 132) was found with values up to 59 mF cm^{-2} that were a function of η . Surprisingly, these authors did not use the interesting reaction model treatment published earlier by Armstrong and Henderson¹²⁹ in the discussion of their results; the large capacitance values

measured were probably related to the pseudocapacitance of adsorbed H (see chapters 3-4).

There are several difficulties in the determination of the behavior of o.p.d. H in the h.e.r. using the a.c. impedance method that are not only due to problems of reproducibility of the surface of active metal electrodes; the following problems also arise: a) H_2 bubbles that are formed cathodically and become detached from the electrode cause a "noise" effect and distortion of the frequency dispersion of the impedance data; b) H_2 and H^+ diffusion at active cathodes may cause complications due to introduction of a Warburg impedance element¹²²; c) the character of the h.e.r., requiring measurements over a wide frequency range to achieve adequate resolution of processes with different relaxation times; and d) problems about the interpretation of the R and C quantities measured (the real, Z' , and imaginary, Z'' , components of the impedance) in terms of Faradaic resistance and pseudocapacitance in the equivalent circuit for the reaction of H_2 evolution involving a potential-dependent coverage of the adsorbed intermediate. This latter important question was dealt with by Armstrong and Henderson¹²⁹ and is further examined in some detail in a later chapter (39) of this thesis.

1.9.3 Potential-decay method

It has been shown in works of Conway, Tilak and the present author that the study of the course of potential decay, V, in time, t ¹³³⁻¹⁴³, after interruption of a polarization current can give information on a) the capacitance behavior of the elec-

trode interface¹³³⁻¹³⁵ and b) on the kinetic and mechanistic behavior of the electrode reaction¹³⁵⁻¹³⁷. From the capacitance behavior, information on potential-dependence of H coverage can be obtained.

The potential-decay method was sometimes used in early electrochemical kinetic studies, e.g. by Butler and Armstrong¹³³ at Hg and by Conway and Bourgault at Ni-oxide electrodes¹³⁵, since the required instrumentation is relatively simple. Previous procedures utilized integration of the differential equation for potential decay, $V(t)$ in time t , giving a $V(t)$ vs $\log t$ plot (see section 3.1). However, when a pseudocapacitance, C_0 associated with potential-dependence of coverage by electroactive intermediates e.g. H, is involved, the decay equation can only be integrated after some assumption is made regarding a limiting form of C_0 as $f(V)$. Also, for some fast reactions, e.g. the h.e.r. at Pt, the transients of potential decay are complete within 0.2 s and could not possibly be accurately and reliably studied by early potential decay measurement techniques using analog oscilloscopes. Attempts to evaluate the "differential capacity"¹³⁸⁻¹⁴² associated with the h.e.r. at nickel, iron and mercury electrodes were made by the potential decay method using either the initial rate of decay of¹³⁸ η , $\left(\frac{d\eta}{dt}\right)_{t=0}$

or the rate of decay, $d\eta/dt$, read from the decay curve at any η ¹⁴². The results were quantitatively different: either only a constant small capacitance at the high η region¹³⁸ was observed or the capacitance was found to be not only a function of η but also a function of the η value prior to interruption

of the current.¹⁴²

A new and very effective method of analysis of the kinetics of the decay of η on open-circuit, based on processing of digitally acquired potential decay data in a computer, has been developed in the present research project and will be discussed in this thesis later (see section 3.1). The method enables, for the first time, the o.p.d. H coverage behavior of electrode potential, together with the associated pseudocapacitance, to be reliably determined at potentials where appreciable faradaic currents for H_2 evolution are passing.

1.9.4 Other physicochemical methods

At the present time, no other very satisfactory methods exist for the determination of o.p.d. H. The infra-red absorption method, which has been successful in gas-solid studies, has severe difficulties associated with the strong absorption of components of most electrolytically conducting solutions, e.g. H_2O , which give rise to too strong a background absorption for small changes of absorption due to the electrochemically formed intermediates to be detected in the electrode-solution interphase. Using infra-red reflectance spectroscopy, Bewick et al.¹⁴⁴ have, however, claimed to have detected a state of adsorbed (u.p.d.) H at Pt, bonded in some way to oriented water molecules.

The electron spin resonance technique has been applied to the examination of the behavior of electrochemically produced free radicals in solution but there are severe intrinsic limitations to extending this method to investigation of radicals such as H adsorbed at surfaces. These problems arise from the limited quantity of radicals available for detection, their

lifetime and the problem that a radical chemisorbed, e.g. at a transition metal, probably does not retain the paramagnetic character that it normally exhibits in the free state.

Use of an ellipsometer to measure the polarization of reflected light from electrode surface provides a useful method for study of surface films involving precipitation of a solid product formed in the electrode reaction; also the u.p.d. H film at Pt is detectable. However, application to determination of o.p.d. H in the H.e.r. is probably excluded because of the strong influence of H₂ bubbles formed on the electrodes giving rise to optical inhomogeneities.

The radio-labelling techniques, with direct detection through thin electrode films by means of a Geiger counter, offers opportunities for chemical characterization of adsorbed intermediates in certain reactions. This method has been used in work on adsorption of organic molecules and ions but no o.p.d. H determination work is to found in the literature, e.g. using tritium.

Chapter 2

EXPERIMENTAL

2.1 Choice of electrochemical system and methods

The electrochemical reaction of cathodic hydrogen evolution at Ni, Ni-based alloy electrodes in alkaline solution, and Pt and Au electrodes in both acid and alkaline solutions was chosen for the present subject of study, in particular, the involvement of the o.p.d. H in the h.e.r. at these metals.

The h.e.r. is perhaps the most widely studied electrochemical reaction and has been used as a model reaction in the development of electron transfer theories where an ion neutralization with atom transfer also takes place. Unlike the case of the h.e.r. at Hg, general agreement on the reaction mechanisms for the catalytically active and adsorptive metals has not been reached because, amongst other reasons discussed in section 1.7, there is a lack of experimental information on the adsorption behavior of the reaction intermediate, chemisorbed H in various states. Ni, Ni-based alloys and Pt are typical of such metal electrodes that are active for the h.e.r., especially as they are commercially important and widely used in practical electrocatalytic processes, e.g. in water electrolysis, in the chlor-alkali process and fuel cells. The Au electrode was chosen because of its weaker affinity for H, e.g. no u.p.d. of H is observed at this metal, so that the adsorption behavior at the Au interface will be simpler than that at Pt or Ni. It is interesting, therefore, to extend to the overpotential region

the study of the behavior of adsorbed H in the h.e.r. at the Au electrode, in particular to establish if any o.p.d. pseudocapacitance arises for H adsorption at appreciable overpotential.

Since there is no satisfactory method previously existing for the study of o.p.d. species (see section 1.9); methods for study of capacitive behavior, viz. potential decay and a.c. impedance, were chosen for application and development for determination of the o.p.d. H behavior in the h.e.r. at the above types of electrodes.

2.2 Electrochemical system

2.2.1 Electrodes

i) Ni Electrodes: Ni electrodes were made from 0.038 cm diameter high-purity grade wires (Johnson Matthey & Mallory Co.). The Ni wire samples were degreased by refluxing in acetone in a Soxhlet-type extractor for 12 h and then heated and sealed in protective glass bulbs in a stream of purified hydrogen, as described in earlier papers ^{145, 146}. The glass bulbs were broken in situ in the cell with a suitable negative potential being applied before rupturing the bulbs. The geometric areas were ca. 0.3 cm² but were measured exactly in each experiment.

ii) Ni-Mo-Cd plated alloy electrodes: Ni (80%)-Mo(19%)-Cd(1%) composite electrodes were prepared by electrolytic codeposition of Ni and Mo with traces of Cd on to an Fe plate according to the method described in ref. [147], based on a patented procedure¹⁴⁸ for the preparation of high-activity, electrocatalytic materials for H₂ evolution in electrolyser or

chlor-alkali cells. These cathode materials give unusually low H_2 overvoltage behavior with low decadic Tafel slopes (ca. 30 mV per decade of i), especially at elevated temperature, e.g. 363-358 K in chlor-alkali electrolysis technology^{147,148}.

The composition of the Ni-Mo-Cd electrocoated cathodes was checked by X-ray emission analysis in a s.e.m. These electrodes have a nodular cauliflower appearance under the s.e.m. at moderate magnifications [Fig. 2.1 (a)] and some finer-scale structure is observable at higher magnifications [Fig. 2.1 (b)]. The structure is evidently porous as Kr desorption B.E.T. measurement gave a real/apparent area ratio of ca. 450. The geometric surface area is ca. 0.24-0.30 cm², but was measured exactly in each experiment.

iii). Ni-Mo bulk alloy electrode: For comparison, the cathodic behavior at an 80% Ni, 20% Mo bulk alloy, thermally prepared (by the Metallurgy Department, McMaster University), was also examined. The electrodes were prepared by sealing a piece, $d=0.10$ cm, of the Ni-Mo bulk alloy in a glass tube with epoxy resin which was found not to contaminate the system in alkaline solution over reasonably extensive experimental time periods (several hrs). The geometrical surface area was 0.47 cm².

iv) Au electrode: Electrodes were made from Au wires of 99.999% purity, using Johnson Matthey "Grade 1" Au. Appropriate lengths of these wires, of diameter 0.51 mm were first degreased overnight in refluxing acetone in a Soxhlet extractor. After short lengths of Au were flame welded to much longer Ag electric-



Fig. 2.1 S.e.m. pictures of electrocoated Ni-Mo-Cd electrode at two magnifications a) 10 μm scale; b) 1 μm scale.

al-contact wires, a droplet of softglass was melted on to the Au wire and sealed into the end of a soft-glass tube, leaving ca. 3.3 cm of Au wire protruding beyond the end of the tube. The apparent surface area of the Au electrode was 0.52 cm^{-2} . Seals in pyrex glass were found to be unreliable, giving occasional leaks.

v) The rotating disc Pt electrode: The Pt disc electrode (Pine Instrument Co., Grove City, Pa., USA), mounted in Teflon, had a geometric area of 0.45 cm^2 . All current-densities are reported relative to the real area (0.68 cm^2), calculated from the charges under the hydrogen u.p.d. peaks^{78,149} determined by CV in $0.5M \text{ H}_2\text{SO}_4$ at 296K, taking $210 \mu\text{C cm}^{-2}$ for the monolayer H charge, in the usual way.

The purpose of using a rotating electrode was, besides that of increasing mass-transport (cf. the H_2 diffusion effect discussed by Breiter⁷⁷ and Ludwig et al.⁸⁰), to reduce the effects of hydrogen bubbles formed cathodically on the electrode surface which can cause appreciable fluctuations of current at an active electrode. It was found that with a reasonable rotation rate (3600 r.p.m. in our experimental conditions), very reproducible i vs η relations can be established which are independent of further increase of rotation rate.

Especially, in a.c. impedance measurements at active Pt stationary wire electrodes, "noise" problems arise in the experiments which were caused by the presence of cathodically generated H_2 bubbles. However, at a disc Pt electrode rotated at 3600 r.p.m. or greater, "noise" effects were found to be avoided. Also, H_2 supersaturation and associated effects of the kind treated and observed by Breiter⁷⁷ and

Breiter et al.^{74,76} were eliminated by the electrode rotation. Combined with the procedure of anodic activation of the Pt surface (see below) before each series of readings in the a.c. impedance, potential-decay and d.c. polarization experiments, this approach gave excellently reproducible results.

vi) Reference electrode: Potentials of the test electrodes were referred to that of a reversible Pt/H₂ electrode in the same solution. The potential of this reference electrode was communicated to two digital oscilloscopes in tandem through a Tektronix type 0 amplifier in a cathode-follower mode capable of handling frequencies up to the 10 MHz range, equivalent to the time scale of fast decay transients. For convenience, throughout this thesis, cathodic overpotentials are taken with a positive sign as mentioned earlier.

2.2.2 Cell: A conventional three-compartment all-glass cell was used. Sometimes when measurements were required at relatively high currents (ca. 0.4 A), the stopcock between the working and counter electrode compartments could be opened slightly as necessary. Purified H₂ gas was bubbled continuously through the working and counter-electrode compartments. The limiting diffusion current associated with reduction of residual traces of oxygen was shown to be negligible. For cleaning procedures see ref. 149.

2.2.3 Solutions: All solutions were prepared using pyrodistilled water^{149,150} with additional purification by pre-electrolysis

¹⁵¹ However, the latter procedure was found to be unnecessary when pyrodistilled water was used, as reported previously

149. Aqueous carbonate-free NaOH solutions were made up from AnalaR grade NaOH that had been recrystallized in a N_2 atmosphere at low temperature¹⁵² and dissolved in the requisite volume of pyrodistilled water. H_2SO_4 solutions were made up from the BDH Aristar grade acid which, in earlier work, had been found to be of sufficiently high purity as judged by sensitive cyclic-voltammetry results at Pt electrodes.

2.2.4 Gases: Electrolytic grade hydrogen gas was passed through a conventional purification train consisting of a drying agent, $Mg(ClO_4)_2$, molecular sieve, an oven containing Cu turnings and palladized asbestos at 623 K, and charcoal traps maintained at liquid nitrogen temperature^{149,153}. Nitrogen gas was treated as above, except that only Cu turnings were used in the heated oven for deoxygenation. A bright metallic state of the Cu turnings was maintained by periodic regeneration of the Cu by passage of H_2 through the oven.

2.2.5 The iR-drop measurements: The iR-drop between the Luggin capillary of the reference electrode and the working electrode was determined at various current densities by the current interruption procedure¹⁵⁴ using a Nicolet digital oscilloscope. The solution resistance was also measured by means of a.c. impedance using a Solartron frequency analyzer. The resistances involved were 1.5-2.5 Ohm in 0.5M H_2SO_4 and 3.0-5.0 Ohm in 0.5M NaOH solution, depending on electrode geometry and temperature; results of measurements by the two methods were in good agreement and the resistance values could be determined with an accuracy of 2% prior to each experiment. "iR" drop corrections, based

these resistances, were applied in all the polarization measurements.

2.2.6 Activation of Pt electrodes: In the present work, following the purification procedure mentioned above, it was found that pre-electrolysis did not significantly improve the exchange current density (i_0) values and their reproducibility. However, an anodic activation procedure applied prior to each polarization and potential decay run gave excellent reproducibility and consistently high i_0 values^{23,77,80,83}, and the time effects associated with slow impurity adsorption were able to be avoided.

The point-by-point activation procedure was as follows: before each adjustment of the cathodic polarization current and the following interruption of the current for the potential-decay measurements, an anodic potential of +1.3 V E_{H_2} was applied to the working electrode for 30s. The potential was then switched to the required cathodic value and 10s was allowed for the current to reach a stable value. Using a two-channel PAR model 173 potentiostat, the potential could conveniently be switched between these two, cathodic and anodic, values.

It is known^{78,100} that at +1.3 V at Pt in 0.5M H_2SO_4 surface oxidation, but not oxygen evolution, occurs; moreover, successive potential sweeps between 0.05 and 1.50 V gave identical surface process current profiles which means that the state of the Pt electrode was excellently reproducible over that potential region.

For comparison, unactivated electrodes were also investigated. In these cases, initially clean Pt electrodes were kept

cathodically polarized at about $-0.050 \text{ V } E_{\text{H}_2}$ for known times, and the steady-state polarization i vs η data and the potential decay η vs t data were then recorded. For each experiment in this series, the u.p.d. H cyclic-voltammetry profiles were determined (see section 2.3.4). During the periods of constant potential polarization at -0.050 V , the Pt became slowly deactivated, invariably due to accumulation of poisoning species from residual impurities in the solution, notwithstanding the use of high-purity water.

2.3 Methods

2.3.1 Steady-state polarization

In an early part of the work, electrodes were cathodically polarized at various controlled current densities, i , and the corresponding overpotentials, η , were registered by means of a digital millivoltmeter. "Steady-state" values of η were recorded 30 s after each change of i . Since the polarization behavior could be dependent on the periods of time between successive adjustments of potential η in the steady-state polarization measurements, a slow "potential-sweep polarization" method was developed in order to obtain sufficiently highly reproducible and accurate i vs η data that are required for handling the results generated from the potential decay experiments (see below) in the later development of the work.

This potential-sweep polarization method, provided most of the results presented here (for Ni, Ni-Mo-Cd plate and Au electrode). The procedure involved application of a slow potential sweep to the electrodes by means of a potentiodyne system.

(a PAR 173 potentiostat and a Tacussel type GSATP function generator). The currents and corresponding potentials were recorded simultaneously by a two-channel Nicolet digital oscilloscope (Model 206 or 1090 A). Tests were made to show that the sweep-rates (1 mV s^{-1} for Ni, 3.7 mV s^{-1} for Au and 0.24 mV s^{-1} for the Ni-Mo-Cd electrodeposited composite electrodes) gave polarization results that were almost independent of any further diminution of sweep-rate, i.e. virtual "steady-state" conditions had been achieved. The experimental data collected through the Nicolet oscilloscopes were transferred from the oscilloscope memory to a pdp 11/34 computer and stored on discs; the assembled data was then processed, as required, by the computer.

The advantages of the potential-sweep polarization method are, besides giving excellent reproducibility and high accuracy: a) that a very large number (ca. 2000) of i - η pairs of data may be measured conveniently, allowing Tafel slopes and exchange current densities to be very accurately determined. Also, the large data base facilitated reliable derivation of the pseudocapacitance behavior of the H reaction intermediate, when the results were processed in conjunction with open-circuit potential decay data from separate experiments (see section 3.1); and b) that processing of e.g. back-reaction and iR -drop corrections, together with convenient display of the experimental results as well as comparison of these latter with the predictions of possible physical models, could easily be achieved.

2.3.2 Open-circuit potential decay

Following characterization of the Tafel relations by the above procedure, currents were then interrupted by means of a Clare vacuum mercury relay (HGJ2MT 51231 E00) controlled by a suitably debounced micro-switch, which gives a clean interruption of current with no ringing or spike in the potential transient. The potential vs time relaxation transient was recorded digitally by means of a Nicolet digital oscilloscope (Model 206 and/or 1090A). In most experiments, two oscilloscopes were operated in tandem to cover a total of 5 or 6 decades of time change, starting in the μ s region, at the same time maintaining an adequate sampling density in the time data. A wide logarithmic range of the time data also could have been acquired by only one digital oscilloscope but use of the two instruments is preferred for obtaining results of high reliability and accuracy. Thus, two separate transient measurements were made as follows: first, the $\eta \sim t$ data were acquired and thus stored using the faster range of time scales (0.5-100 μ s per point). In this case, the circuit needed to be "open" for less than a few seconds. With this small disturbance, the system came back easily to the controlled steady-state, which was indicated by the both current and potential being almost identical with the respective values before interruption of current. Then a further acquisition and storage of η - t data using a slower time scale was made. Tests were carried out to show that the results acquired by one oscilloscope from two separate transients, following the above procedure, were identical with the

ones measured by two oscilloscopes used simultaneously for the given experimental conditions.

These digitally acquired $\eta(t)$ data were then processed in a pdp 11/34 computer to obtain the kinetic parameters and adsorption information (see section 3.1) after also computing the quantity $d\eta/dt$ by a differentiating sub-routine, this derivative being required (see section 3.1) for evaluation of the o.p.d. H pseudocapacitance.

The great improvement of the method over other previously used procedures lies in being able directly to evaluate $d\eta/dt$ accurately from the experimental $\eta(t)$ data, which is impossible if the transients are recorded on small Polaroid photographs of signals recorded or stored on screens of analogue oscilloscopes, especially in the very short time range. Since the $\eta(t)$ acquired and stored by the Nicolet oscilloscope had sufficient points (ca. 8000 for each decay curve) the $d\eta/dt$ data could be obtained accurately by numerical differentiation in the computer of the accumulated $\eta(t)$ data recorded on the digital oscilloscopes. The data was represented in sequential sections as a linear polynomial fitted by simple linear regression using the least squares method¹⁵⁵. Each of the sequential sections contains 20 to 80 data points depending on the non-linearity of the η -time curves; the correlation coefficients for the most of the derived $d\eta/dt$ data were found to be at least 0.99 in the present work.

For the open-circuit potential decay transient measurements, special attention must be paid to reduce the noise of the primary $\eta(t)$ data, since for the best numerical differentia-

tiation the $\eta(t)$ results must be as noise-free as possible. Very clear η -time decay curves can be obtained by carefully grounding all instruments together with the working electrode and shielding the reference electrode including the wires, as well as removing any strong a.c. noise source from the working area.

2.3.3 A.c. impedance

The system used for measurements consisted of Solartron 1170 Frequency Response Analyzer (FRA) equipped with an 1186 Solartron potentiostat which controlled the cell.

The Solartron affords a rapid and accurate means of measuring a system's frequency response to various input signals. It consists basically of a programmable sinusoidal signal generator and an analyzer. The generator provides an output signal of known amplitude (5 mV in the present case) and frequency which is in the form $A \sin \omega t$. This signal is applied to the electrochemical system to be tested, through the potentiostat.

The response of the electrochemical system to its input signal has a fundamental a.c. component in the form $R \sin (\omega t + \varphi)$. In simple terms, this means that response of the system has an amplitude, R , different from the input amplitude, A , and a phase-angle change, φ , has also occurred. As well as this fundamental frequency term, harmonics due to system non-linearities, together with random noise, will also be present in the system's output.

The function of the analyzer is to accept the electrochemical system's response to the stimulus signal of the generator

using a correlation process, resolving it in terms of R and ϕ , or the inphase (real) and quadrature (imaginary) components, i.e. in terms of Cartesian coordinates (Z' , Z''). The analyzer uses a digital integration procedure to give precise measurements of the system's response in the presence of interfering noise and harmonics.

A program was written for a pdp 11/34 computer to control the FRA, read the data (Z' , Z'') and corresponding frequencies, f) and store them on a disc. The data could then be analyzed and plotted on a graphics screen or an x-y recorder.

The program allowed the frequency to be scanned in a step-wise sequence, at constant d.c. potential, typically from 10 KHz to 0.05 Hz with a variable number of steps per decade (10 for most cases) on a logarithmic scale. The instrument was set to autoscale and the integration time could be varied to provide higher precision in frequency ranges where the signal-to-noise level was low. The whole series of measurements is then repeated for a different d.c. potential, after waiting at least 10 minutes for the system to acquire its new steady-state, or for the electrode to be reactivated (Pt).

Steady-state d.c. currents were also measured at the same time at the various overpotentials for which impedance data were recorded as a function of frequency. They were found to drift within 5% (10% for the Pt electrode in alkaline solution) during the time required to measure the impedance at the low-frequency end of the impedance spectrum.

For each system, the impedances were measured at 6-10 overpotentials but, for simplicity, only the impedance spectra on

the complex-plane at four overpotentials will be shown here in the diagrams which follow in Chapter 4. At each η , at least two runs were carried out; the reproducibility was found usually to be within 2% (5% for Ni and Pt in alkaline solution).

All experimental a.c. impedance results were obtained at 296 K.

2.3.4 Cyclic-Voltammetry

The technique of cyclic-voltammetry^{78,79} (CV) involves sweeping the potential linearly between two limits, under the control of a potentiodyne, at a constant rate and measuring the potential (time)-dependent current response. The series of peaks thus obtained gives both a good qualitative and quantitative picture of the electro-chemical processes occurring over various potential regions, in the case of u.p.d.

Experimentally, u.p.d. H on Pt electrode is easy to study in a reliable way. Some of the measurements of u.p.d. H in the present experiments were made in a slightly different way from those in previous work in this laboratory^{79,150}. For investigating the effects of prior cathodic polarization on coverage by u.p.d. H, the potential of the electrodes was switched to a given cathodic value at which H_2 evolution took place for a known time (t) and then switched back to an anodic value of 0.050 V; 2 min. were allowed for the bubbling of N_2 to remove the H_2 produced in solution during the cathodic polarization. One cyclic V vs i profile was then recorded from 0.050 V to 0.75 V and a reverse one from 0.75 V to 0.050 V, E_H .

Usually it is desirable to employ the first three methods,

i.e. steady-state polarization, potential-decay and a.c. impedance, to get the fullest complementary information on the polarization behavior and, in particular, its rationalization in terms of electrode properties and hydrogen adsorption behavior. Steady-state evaluations alone are quite inadequate for this purpose.

CHAPTER-3

The Principles of Potential Decay and A.C. Impedance

Methods for O.P.D. H Determination

As with the determination of u.p.d. behavior of H, evaluation of coverage and pseudocapacitance associated with o.p.d. H in the h.e.r. requires a non-steady-state method. It was noted earlier in section 1.9 that determination of anodic charging curves from cathodic overpotentials encounters difficulties in the significance and interpretation of the quantities measured. By means of potential decay transients taken from cathodic overpotentials and/or a.c. impedance measurements made at succession of potentiostatically controlled overpotentials, satisfactory information on the behavior of o.p.d. H species in the h.e.r. can be obtained experimentally; with the aid of the theoretical treatments developed or presented in this thesis, such data can be usefully interpreted in terms of potential-dependence of θ_H and C_ϕ , as well as in relation to the kinetics of the multistep process of H_2 evolution.

In this chapter, the principles of the potential-decay and a.c. impedance methods are described in relation to the quantitative experimental evaluation of o.p.d. H behavior.

3.1 Open-circuit potential decay

For an electrode process characterized by a rate equation for the current density i (see eqn. 1.3)

$$i = i_0 \exp(V/b') \quad (3.1)$$

where $b' \times 2.303 = b$, the Tafel slope ($dV/d \log i$) and polarization conditions are such that the back reaction¹⁵⁶ can be neglected. The course of potential decay in time t , $V(t)$, is given by the differential equation

$$-C \, dV/dt = i(V) \quad (3.2a)$$

$$= i_0 \exp[V(t)/b'] \quad (3.2b)$$

where C is the total capacitance of the electrode interface and $i(V)$ is the internal, potential-dependent self-discharge current, which has the same potential-dependence as the steady-state, experimentally measured current-density.¹³³⁻¹⁴⁷ For cases involving electroactive adsorbed intermediates at significant or appreciable coverage θ ($\theta > \text{ca. } 0.05$)*,

$$C = C_{dl} + C_\phi \quad (3.3)$$

where C_{dl} is the capacitance of the double-layer. Equation (3.2) is based¹³² on the behavior of an equivalent circuit comprising a parallel or series/parallel combination of the charge-transfer resistance and the C_{dl} , together with the H pseudo-capacitance, C_ϕ .

*

It is implicit in this representation that C_ϕ and C_{dl} are combined directly in a parallel equivalent-circuit arrangement. This is usually approximately true if the discharge Faradaic resistance is low. A full treatment of this problem is given in other work in progress with D.A. Harrington. Unpublished results of this work confirm that, for most conditions, eqns. (3.3), (3.11) (3.13) provide a satisfactory (within 5%) basis for evaluation of C_ϕ .

In the simplest case of constant C , e.g. $C_0 = 0$ and C_{dl} is to a good approximation a potential-independent constant (see eqn. 3.3), eqn. (3.2b) can be integrated, viz.

$$\int -\exp[-V(t)/b'] dV = \int (i_0/C) dt \quad (3.4)$$

the solution of which involves an integration constant, τ , that usually must be derived empirically^{134,135}; the well-known¹³³⁻¹³⁵ result is,

$$b' \exp(-V(t)/b') = (i_0/C)t + T = (i_0/C)(t + \tau) \quad (3.5)$$

where $T = b'i_0/i$ and $\tau = b'C/i$. Then

$$V(t) = a - b \log(t + \tau) \quad (3.6)$$

where $a = -b \log(i_0/b'C)$

$V(t)$ then changes linearly with $\log(t + \tau)$ with a slope of $-b$, the negative of the Tafel slope, when C is constant with V . From eqn. (3.6), it can be shown that $dV/d \log t = -b$, as $\tau \ll t$ and it is of interest that evaluation of τ for known i_0 and b will also give C (eqn. 3.5).

If the back-reaction is significant, a similar procedure can be applied to the analysis of the potential-decay behavior by writing, instead of eqn. (3.2b), the following (see eqn. 1.3) involving the net current:

$$-C dV/dt = i = i_0 [\exp \beta VF/RT - \exp -(1-\beta)VF/RT] \quad (3.7)$$

which gives, in place of eqn. (3.6), taking $b' = RT/\beta F$ and $\beta = 0.5$

$$\ln [\tanh(V/2b') / \tanh(V_0/2b')] = -(2i_0/b'C) t \quad (3.8)$$

where $V_0 = V(t=0)$, the initial potential at the moment of current interruption.

In the case when the adsorption pseudocapacitance C_ϕ is important, in particular when $C_\phi \gg C_{dl}$ and is potential-dependent, the decay slope, d , and the Tafel slope are characteristically different^{135,136}. If C_ϕ varies e.g. limitingly as $C_0 \times \exp(-V/d'')$ or $C_0 \exp(V/d'')$ for high and low overpotentials, respectively, where C_0 is a constant, introduction of these cases of C_ϕ variation into eqn. (3.4) gives

$$- \exp[-V(t)/b'] dV = i_0/C_0 \exp[\pm V/d''] dt \quad (3.9)$$

respectively, for the two cases of variation of C_ϕ with V stated above. Then it is found that

$$dV / d \ln(t + \tau) = 1 / (1/b' \pm 1/d'') \quad (3.10)$$

Thus, when C_ϕ increases exponentially with V , $dV/d \ln(t + \tau)$ is numerically $> dV/d \ln i$ while when C decreases exponentially with V , the opposite inequality holds. The potential decay method hence gives the directions of capacity dependence on potential over a range of potentials¹³⁵ for the two limiting cases shown above. They correspond approximately to conditions where θ is decreasing from a value near 1 towards 0.5 or from near 0.5 toward zero since C_ϕ has a maximum at or around $\theta = 0.5$.

The problem with integrating eqn. (3.4), when C_ϕ is $f(V)$, is that the form of the latter relation is not really known a priori so that the above limiting exponential forms considered in earlier work from this laboratory¹³⁵, are restricted special or even arbitrary cases.

A new procedure for dealing with experimental $V(t)$ information using the digitally acquired data is proposed in the present work^{92,95}. The approach is to evaluate C_ϕ directly from eqns. (3.2b) and (3.3) using the relation

$$C_\phi + C_{dl} = i_0 \exp[V(t)/b'] / (-dV/dt) \quad (3.11)$$

or, in logarithmic form,

$$\ln(C_\phi + C_{dl}) = - \ln[-(dV/dt)] + \ln i_0 + V(t)/b' \quad (3.12)$$

Plots of $\log (-dV/dt)$ vs. $V(t)$ can be made and $\ln i_0$ and i are known from the corresponding experimentally determined Tafel plots (eqn. 3.1). The new procedure depends on being able to evaluate dV/dt accurately; this is achieved quite precisely by computer differentiation of the digitally acquired $V(t)$ information from the potential relaxation following interruption of current, these data having been recorded as ca. 8000 V, t points.

A more general treatment of the decay data involves the use of the actual (i.e. not necessarily Tafelian) $i(V)$ data from steady-state polarization measurements in the derivation of $C(V)$; this removes the restriction to reactions exhibiting linear Tafel $\log i$ vs. V relationships. In this way, $i(V)$ and dV/dt from separate experimental measurements can be combined (from eqn. (3.2a)) according to

$$C_\phi + C_{dl} = i(V) / (-dV/dt) \quad (3.13)$$

or

$$\log (C_\phi + C_{dl}) = \log i(V) - \log (-dV/dt) \quad (3.14)$$

in order to derive the interfacial capacitance behavior.

Therefore, the C_ϕ as function of V can be directly evaluated from the experimental $i(V)$ and dV/dt data by means of eqn. (3.13) or (3.14) without any empirical parameters being involved or any assumption being made about the form of the adsorption

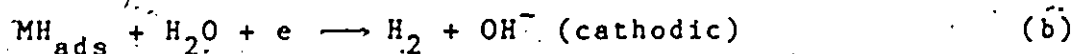
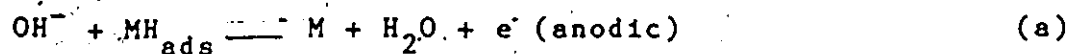
isotherm for the electroactive species characterized by C_ϕ or even without knowing the specific form of the rate equation for the reaction. It is noticed that since both $i(V)$ and dV/dt in eqn. (3.13) are the actual experimentally measured quantities, the back reaction correction, e.g. as for the case of eqns. (3.7) and (3.8), is also avoided.

From the derived C_ϕ vs V data, the coverage or changes of coverage of the o.p.d. H species involved in the reaction can be calculated as $f(V)$ by integration of the experimentally determined C_ϕ vs V profile (see eqn. 1.17).

Eqns. (3.11-3.14) give information about the total electrode interface capacitance, $C_\phi + C_{dl}$. Only the term C_ϕ is of interest in the electrode kinetics and adsorption behavior of H, i.e. when $C_\phi \gg C_{dl}$. As we shall see, the significant results of the above treatment are readily recognized: (i) when $C_\phi \gg C_{dl}$ and is potential-dependent and (ii) when $C = C_\phi + C_{dl} \rightarrow$ constant, equal to the value of C_{dl} .

When $C = C_{dl}$, potential relaxation takes place (cf. refs. 133, 136) by self-discharge of the double-layer capacitance through continuing passage of electronic charge across it at a rate determined by the potential-dependent Faradaic reaction resistance as characterized by the charge-transfer kinetics.

When $C_\phi \gg C_{dl}$ and the electrode surface is appreciably covered by the reaction intermediate, e.g. H, the self-discharge process must proceed by mixed anodic and cathodic reactions, viz, for the h.e.r. in alkaline solution



since the charge for H removal at appreciable coverages is on the order of 25 times greater than the charge required for changing the potential difference across C_{dl} over the range of $\eta(t)$ during decay.

When $C_s \gg C_{dl}$ it is presumed, in the usual way (cf. refs. 25, 68), that a desorption step (e.g. b) is rate-controlling in the overall reaction so that the partial reaction process (a) is almost in equilibrium. On open-circuit decay¹³³⁻¹³⁶ it is reasonable to assume that the same conditions must obtain, i.e. with step (b) continuing to be rate-controlling so that the same values of i_0 and b apply in equation (3.2) as they do in the corresponding Tafel equation for the steady-state process. The equivalent circuits involved were discussed by Tilak and Conway in ref. 136.

The relation between Tafel slope b and potential-decay slope d ($d = d \log (-dV/dt)/dV$) can be derived from eqn. (3.12)

$$d \log C(V) / dV = 1/d - 1/b \quad (3.15)$$

From eqn. (3.15), it is clear that, when $d=b$, $d \log C(V)/dV = 0$, i.e. the interfacial capacitance is independent of potential (see eqn. 3.4); when $d > b$, $d \log C(V)/dV > 0$, i.e. the capacitance increases as the potential is numerically increased while when $d < b$, $d \log C(V)/dV < 0$, i.e. the capacitance decreases as the potential is increased. These cases correspond to the ones referred to earlier in this section with regard to the

relation between the Tafel and decay slopes.

Typical potential decay results can be illustrated as shown in Fig. 3.1: when the potential is high enough ($C_\phi \rightarrow 0$), experimentally both $\log i$ and $\log (-dV/dt)$ vs V should be parallel straight lines with slopes $b = d_2$ (see Fig. 3.1) and the separation between the two lines is determined by $\log C_{d1}$ (see eqns. (3.12), (3.14) and (3.15)). When the potential is low, C_ϕ becomes significant and $b > d_1$ (C_ϕ decreases as potential is increased in this case, see eqn. 3.15). The quantity $C_\phi + C_{d1}$ can be evaluated as $f(V)$ by eqns. (3.13) or (3.14); if the values of i and dV/dt at each V have been obtained by numerical interpolation and differentiation.

Following the above discussion, the critical experimental conditions in using the potential decay method are:

- (i) Beside the charge-transfer processes and adsorption or desorption of reaction intermediate(s) in the studied reaction, there should be no other reaction occurring during the course of the potential decay measurement, e.g. corrosion of the electrode, adsorption and desorption of impurities, etc.
- (ii) In the case of the h.e.r., constant H_2 pressure must be maintained, e.g. by bubbling H_2 since potential is also a function of H_2 gas pressure.
- (iii) The Tafel polarization and potential decay results must be reproducible and the two types of measurements must be made under identical experimental conditions, one after the other.

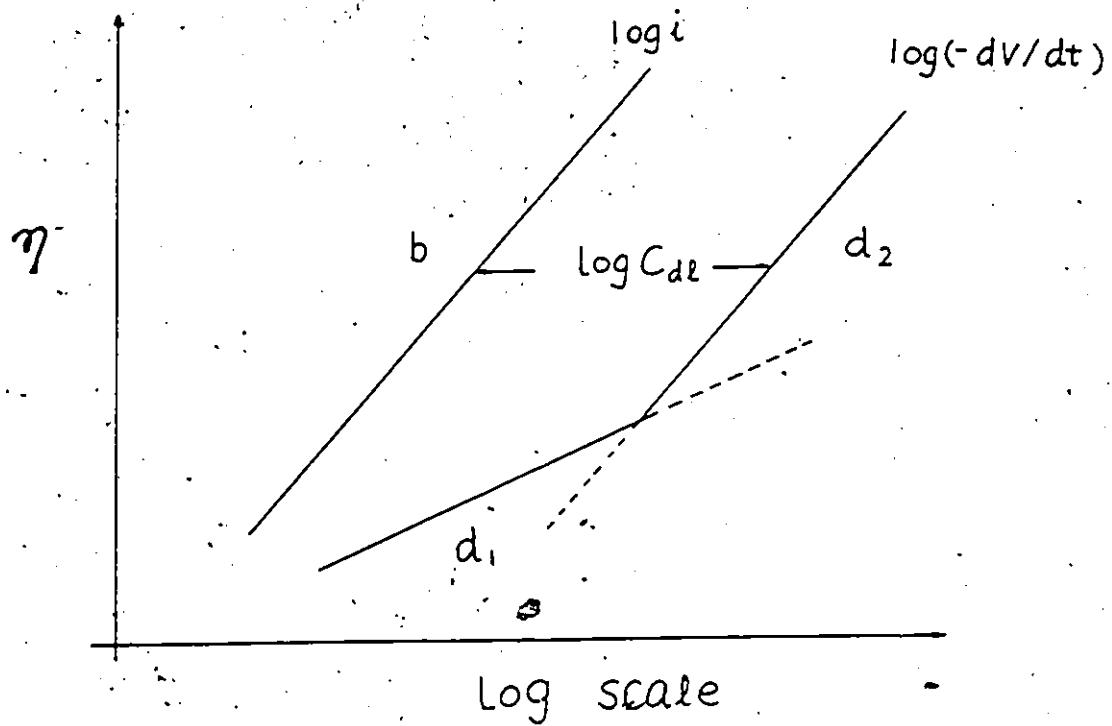


Fig. 3.1 Schematic representation of the $\log i$ and $\log(-dV/dt)$ vs η plots. Region of slope d_1 corresponds to $C_0 > C_{dl}$.

In eqns. (3.11 - 3.14), it is implicit that C_{dl} and C_ϕ are added in a simple parallel relationship but sometimes this is an oversimplification. In that case a fuller analysis of the relaxation characteristics of the equivalent circuit must be made, as for an impedance analysis (see below). This matter has been thoroughly examined in related work with Harrington in this Laboratory and some of the conclusions will be brought into the discussion of the results later in Chapter 4.

3.2 A.c. impedance method

3.2.1 Complex-plane and Bode plot representation

Cole and Cole¹⁵⁷ studied the relaxation or dispersion effect of the dielectric polarization in a polar medium and for the first time expressed their results in terms of a plot of the real vs the imaginary component of the dielectric constant, giving a so-called Argand diagram or a representation of the kinetic behavior in the "complex-plane." It was recognized by Rehbach and Sluyters¹⁵⁸ in 1961 that a similar representation could be applied to the kinetic behavior of electrode processes, where a "real" (ohmic) component arises, corresponding to the reciprocal of the dependence of the rate on potential over a small modulation potential, together with an "imaginary" (capacitive) one, dependent on frequency. The complex-plane method of analysis has been very fruitful in the treatment of kinetics of surface and other processes at electrodes, e.g. by Armstrong et al.^{129,159} and by Epelboin and Keddam et al.^{124,125,160}

The a.c. impedance data are usually analyzed in terms of a proposed "equivalent circuit" of the electrochemical interface and, in earlier work, the elements of the circuit, viz. double layer capacitance, charge-transfer resistance, pseudocapacitance and Warburg impedance¹⁶¹, have been identified, not always correctly, with parameters of the constituent steps of the reaction mechanism.

In the complex-plane representation of the a.c. behavior, the capacitive contribution, Z'' , to the impedance Z is plotted against the ohmic one, Z' , for various frequencies, f . Z' and Z'' are read out directly from the Solartron frequency response analyzer used in present work.

Regular simple kinetic processes occurring across an interface exhibiting a double-layer capacitance give a semicircular arc lying on the ohmic resistance axis (Fig. 3.2a) while complex processes, with more than one characteristic rate constant, give two or more arcs (Fig. 3.2b). Processes coupled with diffusion which give rise to a Warburg impedance generate a straight line of 45° slope in the complex-plane plot (Fig. 3.2c) since the capacitive and ohmic contribution arising from diffusion are each linearly dependent on $\omega^{-1/2}$ ($\omega = 2\pi f$) and thus exhibit a phase-angle of 45° , independent of f .

Some processes that involve generation of a surface film which can give rise to passivation exhibit an S-shaped i vs. V profile. This behavior leads to negative resistance and negative capacitance which corresponds to a pseudoinductance. In the complex plane, such processes give (cf., ref. 124, 125, 160)

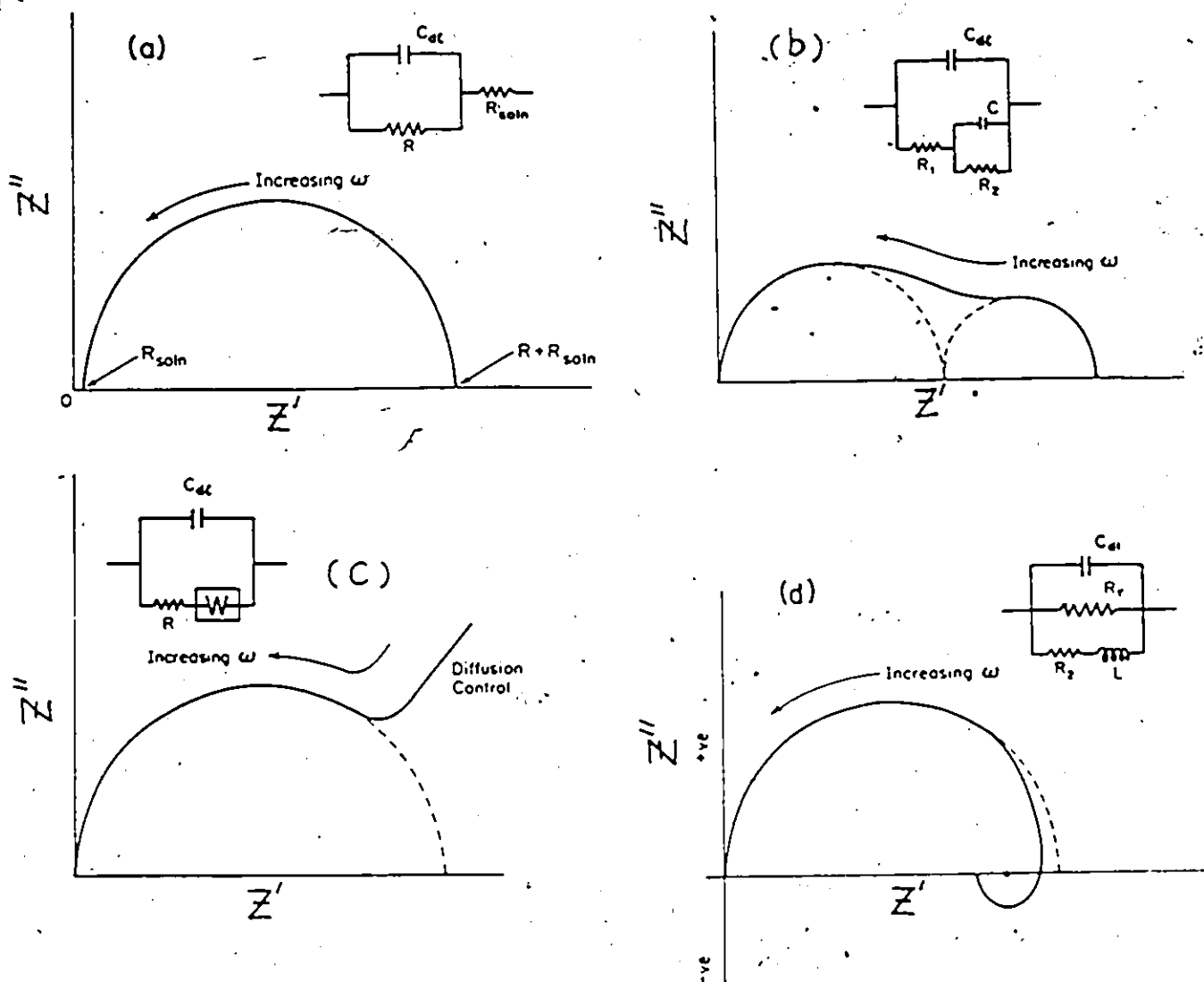


Fig. 3-2 Plots of capacitive (Z'') vs ohmic (Z') impedance components in the complex plane for various types of electrochemical process: (a) a regular reaction with a reaction resistance R at an electrode with double-layer capacitance C_d ¹²²; (b) a two-stage reaction involving, e.g., discharge and another surface reaction^{129,159}; (c) a process involving a reaction resistance R with diffusion Warburg impedance; (d) a process coupled with surface reactions giving instability corresponding to a pseudoinductance^{124,125}.

curves such as that in Fig. (3.2d), with a loop.

The parameters may be calculated from the diameters of the circles (R) or the critical (resonant) frequency (ω^*) of the the experimental point at the top of the arc ($C = 1/\omega^* R$). This method of estimation of the parameters is prone to some unavoidable error because it uses only a few experimental points, and because the theoretical curves may not always be true circles.

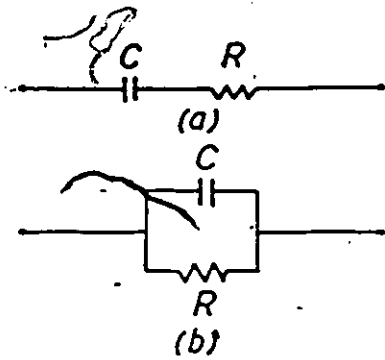
A more rigorous method of impedance plane analysis involves examining a series of value of the parameters of the model, e.g. the rate constants, until the theoretical impedance locus best matches all the experimental data. In the present work, the latter approach was used.

An alternative method for interpretation of complex impedance data can be obtained using the so-called Bode plot¹⁶². Since:

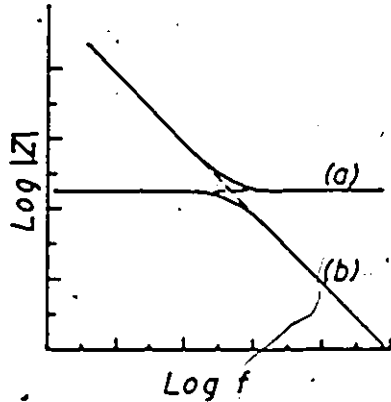
$$\ln Z = \ln(X + jY) = \ln(|Z|e^{j\phi}) = \ln |Z| + j\phi \quad (3.16)$$

where ϕ is the phase angle, a plot of both the logarithm of $|Z|$ and of ϕ vs $\log[\text{frequency}]$ is required for a proper description of the impedance behavior.

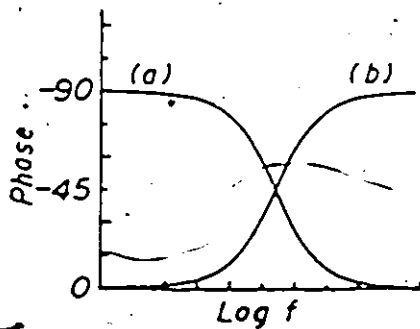
In a Bode plot, the impedance as $f(\omega)$ of a "perfect capacitance" can be represented as a straight line with a slope of -1 and a phase angle of -90° (see Fig (3.3)). The behavior of a "resistor" will plot as a horizontal line for the $\log |Z|$ with a phase angle of 0° (see Fig (3.3)). A Warburg impedance will give a straight line with a slope of $-\frac{1}{2}$ and a constant phase-angle of -45° . While the essential information is present



A. Simple RC circuit configurations:
(a) in series; (b) in parallel.

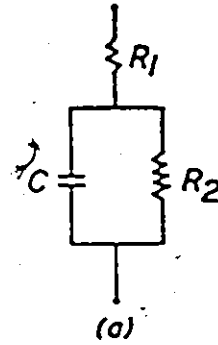


B. $\text{Log } |Z|$ vs $\text{log } f$ for the circuits shown in A.

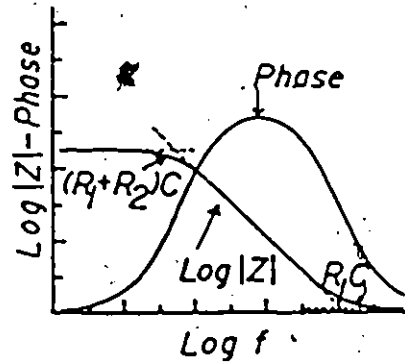


C. The phase angle vs $\text{log } f$ for the circuits shown in A.

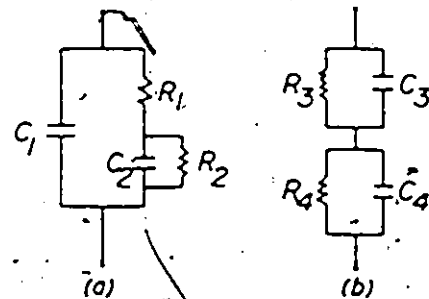
Fig. 3.3 Schematic representation of the equivalent circuits (A; D and F) and the corresponding Bode plots (B, C; E and G).



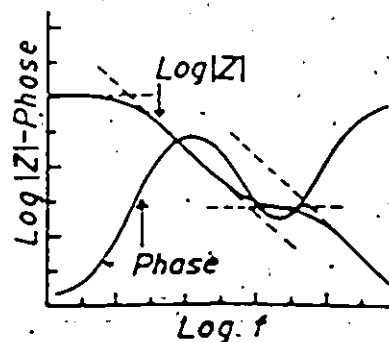
D. The circuit of a parallel RC in series with a simple R.



E. Bode plots for circuit in D.



F. Two different circuits with identical characteristic Bode plots.



G. The Bode plots for both circuits in F.

in a complex-plane plot when the frequencies are labelled on the graph, the Bode plot provides an alternative way of treating the experimental data in relation to theoretical models, especially as it shows more clearly than in the complex-plane method, the frequency-dependence which is very important for capacitance determination.

Typical Bode plots and corresponding equivalent circuits are illustrated in Fig. 3.3. In the present work, for simplicity, only $\log |Z|$ vs $\log \omega$ plots will be shown in most cases.

3.2.2 Theory of a.c. impedance behavior for a multi-step process with one adsorbed intermediate

A.c. impedance data can also be directly analyzed in terms of the rate-constants and adsorption isotherm parameters for the elementary steps of the mechanism. A rather generalized but useful treatment of a two-step reaction with one adsorbed intermediate has been given by Armstrong et al.^{129, 130}. In the present work*, Armstrong's treatment has been extended to the multi-step, single or two adsorbed intermediate(s) case, and applied to the case of the h.e.r.; especially, in the present work, the behavior of the o.p.d. H generated in the h.e.r. was, for the first time, successfully determined by analyzing the

* The work reported here is in collaboration with Dr. D.A. Harrington and is based on a joint paper to be published with him (see refs. 96-98).

a.c. impedance data. This approach was conducted to provide an analysis complementary to that involved in evaluating the behavior of the o.p.d. H by means of the potential decay method (section 3.1).

The usual general reaction mechanism for the h.e.r. is considered: electrosorption (Volmer reaction, eqn. (1.6)) followed by a parallel electrodesorption (Horiuti reaction, eqn. (1.7)) and recombination desorption (Tafel reaction, eqn. (1.8)). The particular reaction mechanism for an electrochemical system characterized by the magnitude of the rate constants for each step and their potential-dependence. The rate constants were evaluated by analyzing the a.c. impedance data coupled with information from steady-state polarization measurements. (see discussion below).

A traditional assumption in the electrochemical study of a multi-step reaction is that^{24,26} there is always a recognizable "rate-determining step" (r.d.s.) which characterizes the kinetic behavior of the reaction. Consequently, the other reaction steps, prior to the r.d.s., were regarded as in quasi-equilibrium; then the adsorption isotherm of reaction intermediates on the electrode surface can be evaluated for the quasi-equilibrium condition. This assumption is, however, sometimes oversimplified as indicated in the present study and by other authors¹⁶⁰. On the contrary, in the present work, the kinetics of the h.e.r. are described precisely in terms of the rate constants for the individual steps in the reaction mechanisms. Also, the steady-state coverage θ_{ss} as a function of η can be calculated for the mechanism with indicated rate constants without any

"quasi-equilibrium" assumption. A corresponding steady-state pseudocapacitance, C , arises as treated by Gileadi and Conway³⁷⁻⁴⁰ and characterizes the potential-dependence of θ_{ss} for various steady-currents at different polarization, η values.

3.2.2.1 General derivation and equivalent circuits

If we use v_1 , v_2 , v_3 to denote the net rates (in $\text{mol cm}^{-2} \text{s}^{-1}$) of steps 1.6, 1.7, and 1.8 (on page 6-7) in the directions written, then the Faradaic current may be found by solving eqns. (3.17) and (3.18) for the potential program of interest:

$$i/F = r_o = v_1 + v_2 \quad (3.17)$$

$$(q_1/F) d\theta/dt = r_1 = v_1 - v_2 - 2v_3 \quad (3.18)$$

In these equations, r_o is the net rate of production of electrons, r_1 is the net rate of production of the adsorbed species, θ is again the fractional surface coverage of the adsorbed intermediates and q_1 is the charge for complete coverage. v_3 is defined as the rate of hydrogen production in step 1.8, or half the rate of consumption of θ in that step, with the consequence that the coefficient two appears in equation (3.18). It is assumed that mass transport of species towards or away from the electrode surface is not rate-limiting, i.e. r_o and r_1 are functions of θ and E only.

Equation (3.19) gives the applied potential, consisting of the d.c. or steady-state potential and the small amplitude sinusoidal a.c. component. Both i (3.21) and θ (3.20) will vary sinusoidally also, but with different amplitude and phase

(contained in Δi and $\Delta \theta$):

$$E = E_{ss} + \Delta E \exp(j\omega t) \quad (3.19)$$

$$\theta = \theta_{ss} + \Delta \theta \exp(j\omega t) \quad (3.20)$$

$$i = i_{ss} + \Delta i \exp(j\omega t) \quad (3.21)$$

Under small perturbations from equilibrium, the rates may be expanded in Taylor series form, neglecting second and higher order terms:

$$r_o = r_{o,ss} + (\partial r_o / \partial E)_\theta (E - E_{ss}) + (\partial r_o / \partial \theta)_E (\theta - \theta_{ss}) \quad (3.22)$$

$$r_l = r_{l,ss} + (\partial r_l / \partial E)_\theta (E - E_{ss}) + (\partial r_l / \partial \theta)_E (\theta - \theta_{ss}) \quad (3.23)$$

In order to simplify the material which follows, it is convenient to define three parameters A, B, and C, as:

$$A = F(\partial r_o / \partial E)_\theta \quad (3.24a)$$

$$B = F^2/q_l (\partial r_o / \partial \theta)_E (\partial r_l / \partial E)_\theta \quad (3.24b)$$

$$C = -F/q_l (\partial r_l / \partial \theta)_E \quad (3.24c)$$

An expression for $\Delta \theta / \Delta E$ may then be obtained by substituting eqns. (3.20) and (3.22) into eqn. (3.18):

$$\Delta \theta / \Delta E = (\partial r_l / \partial E)_\theta / [j\omega q_l / F + (\partial r_l / \partial \theta)_E] \quad (3.25)$$

The Faradaic admittance, $Y_f = \Delta i / \Delta E$ may finally be obtained by using eqns. (3.17), (3.19)-(3.25):

$$Y_f = A + B/(j\omega + C) \quad (3.26a)$$

$$Y_f = 1/R_\infty + 1/[R_o(1 + j\omega t)] \quad (3.26b)$$

$$Y_f = [R_\infty + 1/(1/R_p + j\omega C_p)]^{-1} \quad (3.26c)$$

where $R_{\infty} = 1/A$; $\tau = 1/C$; $R_0 = C/B$

$$R_p = -B/[A(CA + B)] = -R_{\infty}^2/(R_0 + R_{\infty}); C_p = -A^2/B = -R_0\tau/R_{\infty}^2 \quad (3.27)$$

The several forms of eqn. (3.26) are identical: (3.26a) is the simplest, (3.26b) conforms closely with Armstrong's notation which will be used in the later discussion, and (3.26c) can be directly written out from the equivalent circuit shown in Fig. (3.4).

The double-layer capacity can be taken into account by inserting it in parallel with the faradaic process, in accordance with the usual simplification concerning the separability of faradaic and non-faradaic processes, and the total interfacial impedance, Z , is then as given by

$$Z = 1/(Y_f + j\omega C_{dl}) \quad (3.28)$$

The real, Z' , and imaginary, Z'' , components of total impedance Z are:

$$Z' = Y'/(Y'^2 + Y''^2), \quad Z'' = Y''/(Y'^2 + Y''^2) \quad (3.29)$$

where

$$Y' = 1/R_{\infty} + 1/R_0(1 + \omega^2\tau^2)$$

$$Y'' = \omega[C_{dl} - \tau/R_0(1 + \omega^2\tau^2)]$$

The resulting function (eqn. 3.28 or 3.29) may be plotted in the complex impedance plane. The possible shapes of this function have been given by Armstrong: they approximate to two semicircles, either both above the real axis or one above and one below this axis. Under appropriate limiting conditions, these may appear merged into one semicircle.

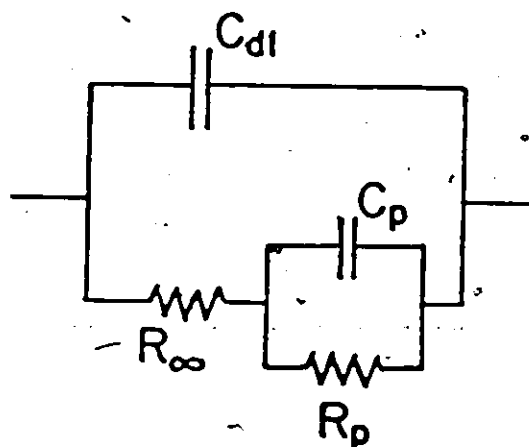


Fig. 3.4 Armstrong's equivalent circuit for one adsorbed intermediate.

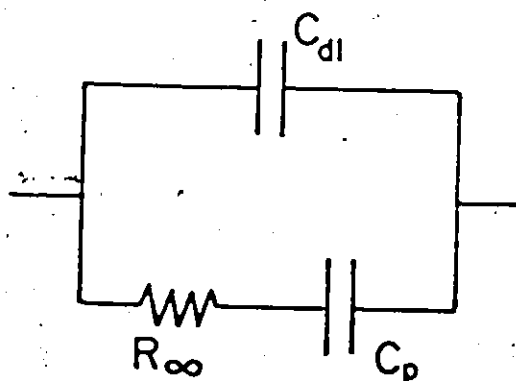


Fig. 3.5 The equivalent circuit for the u.p.d. case.

The form of eqn. (3.26) was derived quite generally, without regard to the actual potential-dependence of r_0 or r_1 , or the isotherm for the adsorbed species. Consequently, any reaction-mechanism with one adsorbed intermediate and without diffusion control will give impedance behavior with a frequency dispersion governed by eqn. (3.26).

Quite generally, there may be several equivalent circuits for the same mechanism, but the equations describing their frequency dispersion will simply be different forms of the same equation. The equivalent circuit expected on intuitive grounds may be incorrect. In the present case, the circuit of Fig. 3.4 is often proposed with the interpretation that R_∞ is the charge-transfer resistance of the electrosorption step, R_p is the charge-transfer resistance of the electrodesorption and recombination steps and C_p is the pseudocapacitance of the adsorbed species. However, it is clear from the above derivation that R_∞ and R_p are each properties of two or more steps in the reaction. Also, as will be shown later, C_p may not, in fact, be identified with what is usually called the pseudocapacitance, but is related to it in a rather complicated way.

3.2.2.2 Significance of parameters

(a) The parameter τ

As noted by Armstrong, τ is a time constant, which measures how rapidly θ relaxes to its new value after the potential is changed. This has a quite precise meaning in the case where the rates are linear in θ , such as for the h.e.r. under Langmuir

conditions with negligible recombination. In this case, if the potential is stepped to a new potential E_{ss} then θ relaxes exponentially to its final value with the time constant τ , the same value that would be obtained in an a.c. impedance experiment at an applied d.c. potential E_{ss} . (This may be shown by solving the differential eqn. (3.18) for constant potential conditions). In more complex cases, such as the h.e.r. with the recombination step considered, the relaxation will not be exponential though we may non-rigorously attach a similar significance to τ .

(b) Pseudocapacitance and C_p

The pseudocapacitance, C_p , and the equivalent circuit element C_p both have the dimensions of capacitance. They will be discussed in turn. In order to calculate the pseudocapacitance, the steady-state value of θ at any d.c. potential E_{ss} is first found by setting eqn. (3.18) equal to zero and solving for θ as a function of potential. Differentiation of this function and multiplication by q_1 gives the quantity C_p called the pseudocapacitance by several authors. Extensive discussion of the θ_{ss} and C_p functions was given by Conway and Gileadi³⁷⁻⁴⁰.

Since r_1 is zero at every steady-state potential, its derivative with E_{ss} is also zero (eqn. (3.30)), leading to an alternative formula for the steady-state pseudocapacitance (eqn. (3.31)):

$$dr_1/dE_{ss} = 0 = (\partial r_1 / \partial \theta)_E d\theta_{ss}/dE_{ss} + (\partial r_1 / \partial E)_\theta \quad (3.30)$$

$$C_p = q_1 d\theta_{ss}/dE_{ss} = -q_1 (\partial r_1 / \partial E)_\theta / (\partial r_1 / \partial \theta)_E \quad (3.31)$$

Because the derivative $(\partial r_1 / \partial E)_\theta$ in this expression appears in combination with another derivative in B [eqn. (3.24b)], the pseudocapacitance at a given potential cannot be obtained directly from the impedance parameters at this potential. It can, of course, be calculated from the rate-constants once these are obtained from a full analysis of the potential-dependence of the parameters. This latter method has the disadvantage that a specific reaction scheme must be assumed.

It should be noted that the quantity $q_1 d\theta / dE$ depends on the potential program applied to the interface; for example, it has different values in a cyclic-voltammetry experiment than in steady-state current-potential measurements. The above definition as derivative of the steady-state θ vs E curve is the one used by most authors, although different quantities have been defined as pseudocapacitance in the literature, e.g. peak current divided by sweep-rate in cyclic-voltammetry or the value of a capacitance in an experimentally evaluated equivalent circuit.

The second quantity with dimensions of capacitance, C_p :

$$C_p = -A^2/B = -q_1 [(\partial r_0 / \partial E)_\theta]^2 / [(\partial r_0 / \partial \theta)_E (\partial r_1 / \partial E)_\theta] \quad (3.32)$$

may also be compared with the steady-state pseudocapacitance (eqn. (3.31)) and it is seen that these two quantities are not, in general, equal. C_p is a pure capacitance and, in view of the preceding discussion, cannot be a true measure of the variation of adsorbed charge with potential under a.c. conditions, i.e., charge on its "plates" is not the same as the adsorbed charge,

and therefore it is not identical with C_ϕ . Rather, it results from the artificial requirement that an equivalent circuit must contain only linear elements, i.e. pure capacitors, resistors and inductors. C_p appears in combination with the resistor R_p (see Fig. 3.4) so that the combination correctly models the phase delay of the reaction scheme. We do not therefore expect to be able to ascribe too much physical significance to it.

In the case of the h.e.r. C_p and C_ϕ are surprisingly similar in certain potential regions (see below and Fig. 3.6). We therefore seek criteria for the similarity of these two functions.

Comparison of the two equations shows that they will be approximately identical if r_0 and r_1 are comparable [strictly, $(\partial r_0 / \partial E)_\theta \approx (\partial r_1 / \partial E)_\theta$ and $(\partial r_0 / \partial \theta)_E \approx (\partial r_1 / \partial \theta)_E$]. This will arise if the adsorbed species is formed in an electron transfer step and other steps involving charge transfer or adsorbate reaction are much slower. In this case, r_0 and r_1 will each be approximately equal to the rate of the fast step. In the case of the h.e.r., it may be seen from eqns. (3.17) and (3.18) that the rate constants for electrodesorption and recombination must be much smaller than that for electrosorption. One case in which C_p and C_ϕ are exactly equal is in underpotential deposition processes, e.g. of hydrogen, where the adsorbate is formed and removed with accompanying electron transfer in only one step ($r_0 = r_1$). Mathematically, this may be considered a special case of the h.e.r. with $v_2 = v_3 = 0$, although the adsorbed species in underpotential deposition may be chemically and/or configurationally different from that adsorbed in the overpotential region.

In the case of u.p.d. both capacitative quantities, C_p and C_ϕ are identical, and furthermore it is seen from eqn. (3.27c) that R_p becomes infinite, so that the equivalent circuit becomes that of Fig. 3.5.

(c) Resistances

The significance of A or its reciprocal R_∞ is contained in eqn. (3.24a); it is the partial derivative of the steady-state current vs potential relation at constant surface coverage. This quantity is not the same as the derivative of the steady-state current-potential curve, as may be seen by differentiating eqn. (3.17) for steady-state conditions:

$$\begin{aligned} di_{ss}/dE_{ss} &= Fdr_o/dE_{ss} = F(\partial r_o/\partial E)_\theta + F(\partial r_o/\partial \theta)_E d\theta_{ss}/dE_{ss} \\ &= 1/R_\infty + F/q_1(\partial r_o/\partial \theta)_E C_\phi \\ &= \lim Y_f \text{ as } \omega \rightarrow 0 \end{aligned} \quad (3.33)$$

The slope of the steady-state current-potential curve is seen to differ from $1/R_\infty$ by a term involving the pseudocapacitance. Once again, the pseudocapacitance cannot be found from the other measurable quantities in this equation because it occurs in combination with the partial derivative, $(\partial r_o/\partial \theta)_E$; C_ϕ is only accessible if a full kinetic analysis is undertaken.

Equation (3.33) expresses how the increase in steady-state current which occurs with a small increase potential may be decomposed into two parts: the increase due only to increase in potential without allowing the coverage to change (first term) and the additional increase which arises as the coverage is allowed to relax to its steady-state value at the new poten-

tial (second term). Both of these parts are associated with energy dissipation and can therefore be represented by resistors. R_∞ is associated with the charge-transfer at constant coverage:

$$1/R_\infty = (\partial i_{ss} / \partial E)_\theta \quad (3.34)$$

R_o is associated with the relaxation of coverage and is related to the pseudocapacitance by

$$1/R_o = F/q_1 (\partial r_o / \partial \theta)_E C_\phi \quad (3.35)$$

The total faradaic resistance, R_f is the parallel combination of these two or alternatively the series combination of R_∞ and R_p :

$$1/R_f = di_{ss}/dE_{ss} = 1/R_\infty + 1/R_o = 1/(R_\infty + R_p) \quad (3.36)$$

Therefore, the total admittance consists of two terms (see eqns. (3.33) and (3.36)), the first term is $1/R_\infty$ which is frequency independent because the rate can change instantaneously with potential if the coverage does not have to change. The second term represents the relaxation of coverage which is frequency dependent because of the slowness of the reactions.

3.2.2.3 Application to the h.e.r. and the numerical procedure required

Under Langmuir conditions, the rates of reactions (1.6-1.8) are respectively: *

$$\begin{aligned} v_1 &= k_1(1-\theta) \exp(\beta F \eta / RT) - k_{-1} \theta \exp[-(1-\beta) F \eta / RT] \\ &= \lambda_1(1-\theta) - \lambda_{-1} \theta \end{aligned} \quad (3.37a)$$

$$v_2 = k_2 \theta \exp(\beta F \eta / RT) = \lambda_2 \theta \quad (3.37b)$$

* See footnote on following page.

$$v_3 = k_3 \theta^2 = l_3 \theta^2 \quad (3.37c)$$

where l_1 , l_{-1} , l_2 and l_3 are defined obviously in terms of the above equations. The concentrations of H^+ and OH^- have been absorbed into the rate constants. If the usual overpotential scale is chosen for the rate constants, then they are not independent but must be related through the equilibrium constant for the overall reaction:

$$\frac{k_1 k_2}{k_{-1} k_{-2}} = \frac{k_1^2 k_3}{k_{-1}^2 k_{-3}} = 1 \quad (3.38)$$

We may then find r_0 and r_1 (from eqns. (3.17) and (3.18)) and hence the partial derivatives (eqn. (3.24)). These partial derivatives appear in the Taylor series expansion around the steady-state condition and must therefore be evaluated using the steady-state θ . This may be obtained by setting eqn. (3.18) to zero ($r_1 = 0$), neglecting a negative solution which has no physical significance:

$$\theta = -L/4 l_3 + (L^2 + 8 l_1 l_3)^{1/2} / 4 l_3 \quad (3.39)$$

where $L = l_1 + l_{-1} + l_2$, and the pseudocapacitance C_ϕ is given by

$$C_\phi = q_1 d\theta/d\eta = \frac{q_1 \beta F L_N}{4RT l_3} \left\{ \frac{L_p/4 l_3 + l_1/L_N}{[(L_p/4 l_3)^2 + l_1/2 l_3]^{1/2}} - 1 \right\} \quad (3.40)$$

where $L_p = l_1 + l_{-1} + l_2$, $L_N = l_1 - l_{-1} + l_2$

* The rate constants k_{-2} and k_{-3} for the back-reaction can be calculated from eqn. (3.38) but are not independent parameters. Tests show that, unless $k_{-3} > k_3$ and $k_{-2} > k_2$, k_{-3} and k_{-2} will have no significant influence on the simulation, (notice that the back-reaction rates decrease exponentially with increasing η). In the case of the h.e.r. $k_3 \ll k_2$ and $k_{-2} \ll k_2$, e.g. at activated Pt in 0.5 M H_2SO_4 , $k_3/k_{-3} = 300$ and $k_{-2}/k_{-3} = 15$ (see section 4.3.2, Table 4.5), for simplicity, k_{-2} and k_{-3} will not be taken into account in the situations considered here..

The steady-state current is given by

$$i = nF (v_2 + v_3) = 2F(l_2\theta + l_3\theta^2) \quad (3.41)$$

The partial derivative may be substituted back into eqn. (3.24) to get A, B, and C in terms of the rate constants and the overpotential only. Using Armstrong's notation^{78,110} (see eqn. (3.26b)), the quantities R_∞ , R_0 and τ are given by

$$1/R_\infty = F (\partial v_1/\partial E)_\theta + F (\partial v_2/\partial E)_\theta \quad (3.42a)$$

$$1/R_0 = F^2 \tau / q_1 [(\partial v_1/\partial \theta)_E + (\partial v_2/\partial \theta)_E][(\partial v_1/\partial E)_\theta - (\partial v_2/\partial E)_\theta] \quad (3.42b)$$

$$1/\tau = F/q_1 [2(\partial v_3/\partial \theta)_E + (\partial v_2/\partial \theta)_E - (\partial v_1/\partial \theta)_E] \quad (3.42c)$$

where

$$(\partial v_1/\partial E)_\theta = (\beta F/RT)[l_1(1-\theta) + l_{-1}\theta]; \quad (\partial v_2/\partial E)_\theta = (\beta F/RT)l_2\theta;$$

$$(\partial v_1/\partial \theta)_E = -l_1 - l_{-1}; \quad (\partial v_2/\partial \theta)_E = l_2; \quad (\partial v_3/\partial \theta)_E = 2l_3\theta;$$

Armstrong's equivalent circuit (see Fig (3.4)) will be employed and R_p and C_p components are given by

$$R_p = R_f - R_\infty = -R_\infty^2 / (R_0 + R_\infty) \quad (3.42d)$$

$$C_p = -R_0 \tau / R_\infty^2 \quad (3.43)$$

The potential dependences of C_p (eqn. 3.43) and C_ϕ (eqn. 3.40) are plotted in Fig. 3.6 for some selected values of the rate constants, chosen to correspond with those found experimentally (details to be described in Chapter 4). Fig. 3.6 shows that C_ϕ and C_p vs η plots (curve 1) have identical shapes when k_2 and $k_3 \ll k_1$ as discussed in section 3.2.2.1 (b). However,

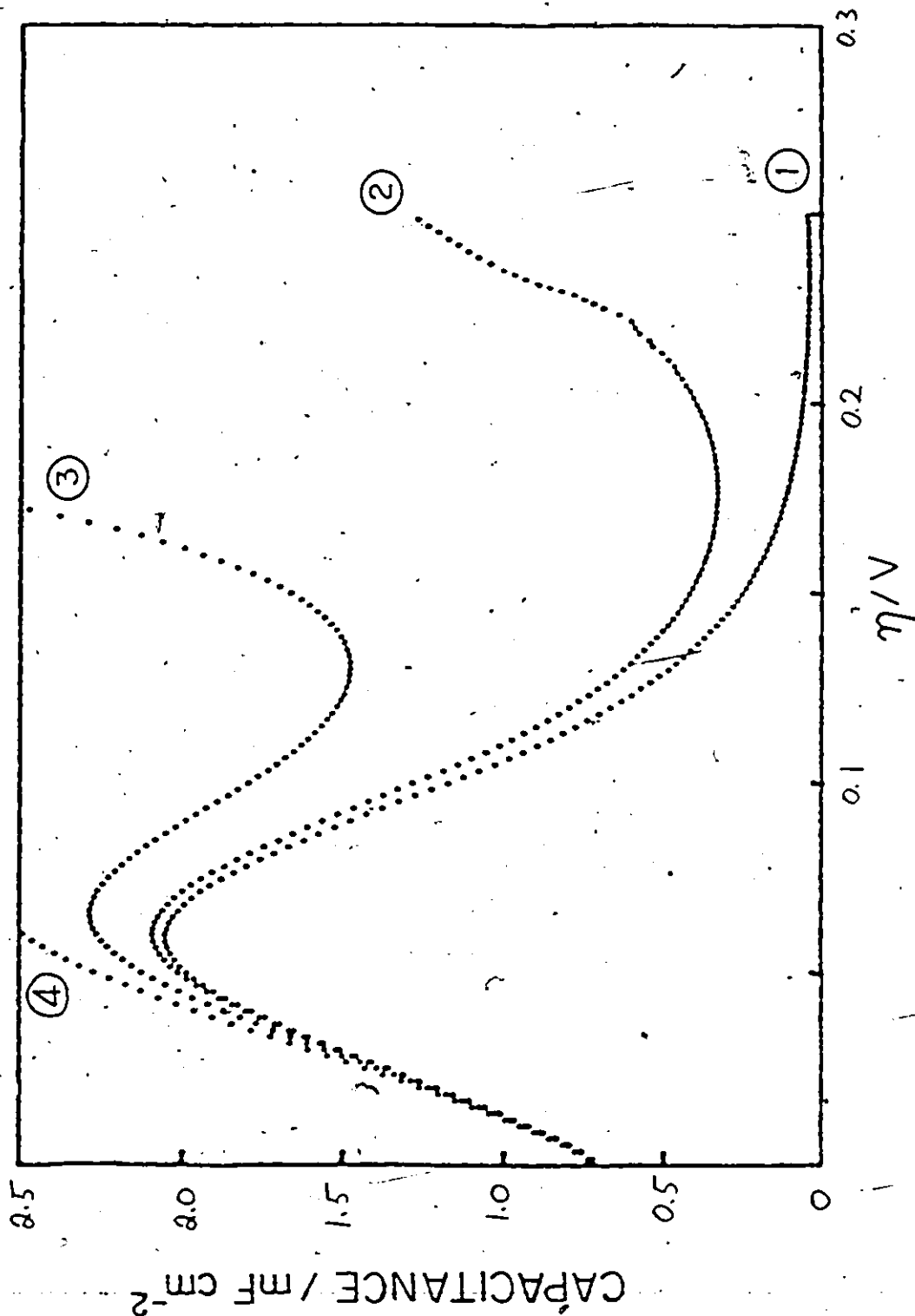


Fig. 3.6 Calculated capacitance vs η/V plots. Curve 1 for both C_1 and C_2 taking $k_1=10^{-8}$; $k_{-1}=10^{-7}$; $k_2=10^{-11}$ and $k_3=10^{-10}$ mol cm⁻² s⁻¹. Curves 2, 3 and 4 are the C_p vs η/V plots taking same rate constants as for Curves 1 except $k_2=2 \times 10^{-10}$; 3) 5×10^{-10} and 4) 10^{-9} mol cm⁻² s⁻¹.

as k_2 becomes significantly close to k_1 , C_p plots (curves 2-4) become deviant from the C_ϕ plot at high η value, increasing exponentially with η instead of approaching zero as does C_ϕ . This shows clearly that C_p does not always have the physical significance of the pseudocapacitance, although it may have values close to C_ϕ in some situations.

Analysis of the data can be carried out by optimally fitting data at a given d.c. potential to eqn. (3.29), modified to include the effect of the double-layer capacitance. The Armstrong circuit is particularly well suited to an initial estimate of the parameters. R_∞ and R_p are approximately the diameters of the high and low frequency semi-circles, respectively, in the complex-plane plots.

A series of values of the rate constants in eqns. (3.37) were manipulated in the computer until, for one set of the k values, sufficiently good agreement was obtained between the numerically evaluated and the experimentally derived values of the a.c. impedance parameters R_∞ , R_p and $R_\infty + R_p$ as $f(\eta)$, (eqn. 3.42), together with the correct representation of the observed steady-state η vs $\log i$ plots for the h.e.r. (eqn. (3.41)).

Then double-layer capacitance, C_{dl} , the charge for full coverage of H , q , the solution resistance, R_s and sometimes the symmetry factor β ($= 0.5$) were modified manually until both simulated complex-plane and Bode-plots, using the same set of rate constants for all d.c. potentials were in sufficiently good agreement. ~~No fitting program for adjusting parameters was~~ used.

A set of the potential-independent rate constants and other parameters must not only fit both the dependence of the parameters of a.c. impedance on η and the dependence of steady-state currents on η , but also the relation between impedance and frequency, i.e. it must reproduce the complex-plane plots and Bode plots at each η . It was found very difficult to establish any other sets of rate constants and parameters to which the same experimental data could be fitted, but it is not possible to state unambiguously that the values given for the kinetic results are the only possible sets.

Chapter 4

RESULTS AND DISCUSSION

For clarity, the four systems studied: bulk Ni metal; electroplated Ni-Mo-Cd composite electrodes; Au and Pt in alkaline and/or acidic solutions, will be treated separately in the three following sections. Since Ni and the Ni-Mo-Cd electrodes have many common properties, they will be discussed together in the first section.

The experimental results to be presented as graphs will mostly be in the form of actual computer print-out points, processed directly from the data sampled in the experiments by means of the digital oscilloscopes (potential-decay) and by means of the Solartron frequency analyzer (a.c. impedance).

4.1 Ni and Ni-Mo-Cd plated electrodes

4.1.1 Results from the potential-decay method

4.1.1.1 Log {current-density} vs Potential Relations

We first refer to the Tafel relations for the Ni, bulk Ni-Mo and electro-plated Ni-Mo-Cd electrodes in 0.2M aq. NaOH in order to characterize the polarization behavior and to evaluate C_ϕ as $f(\eta)$ through equations (3.13) or (3.14). Fig. 4.1 a,b show the η vs $\log i$ plots for Ni wire, bulk Ni-Mo alloy and the 80% Ni-19% Mo-1% Cd composite electrodes at several temperatures. The Ni-Mo-Cd electrodes exhibit two-slope Tafel relations characteristic of a change of mechanism in a consecutive 2 step pathway

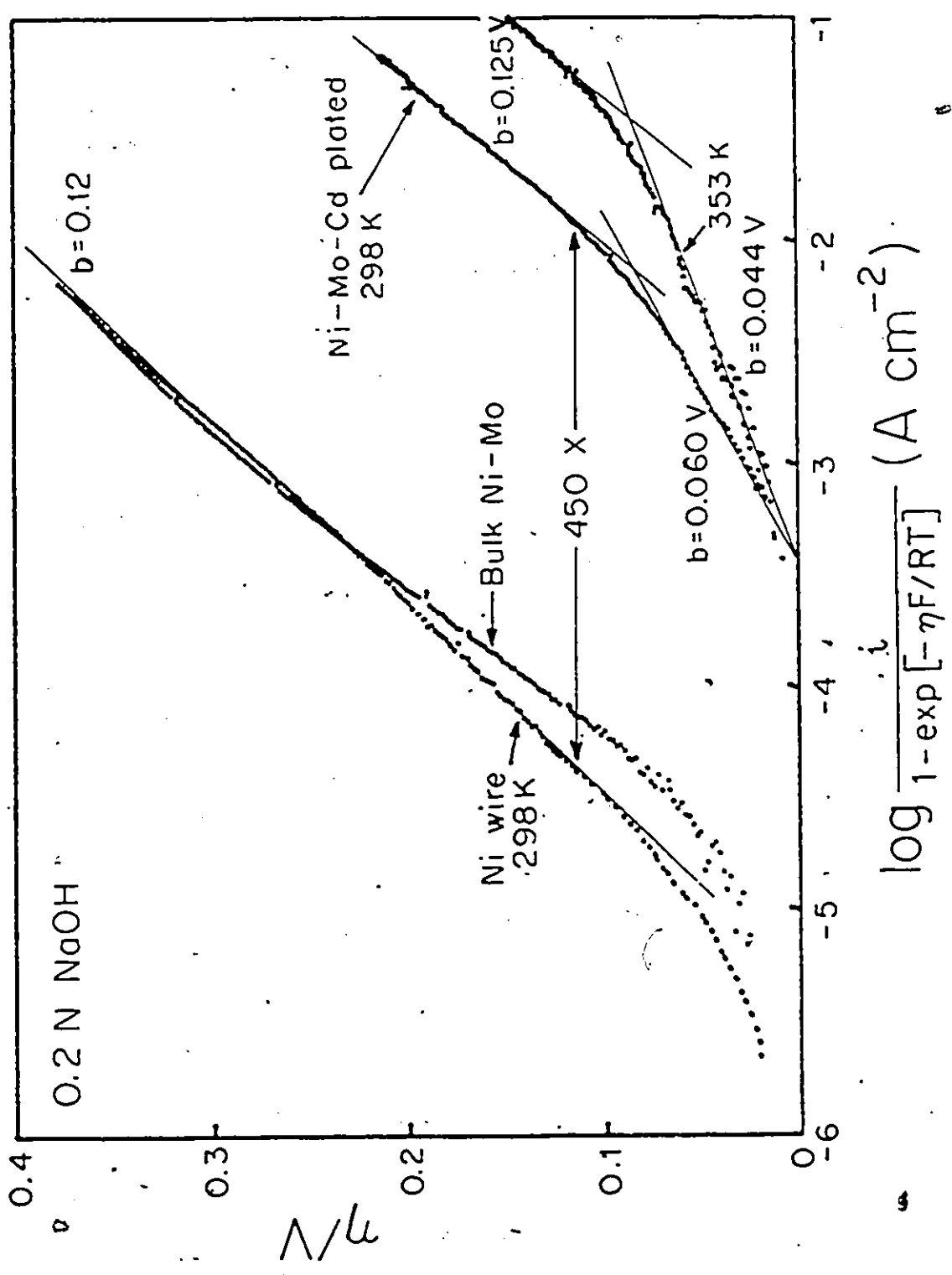


Fig. 4.1 a) Comparative Tafel plots for the h.e.r. on Ni wire and bulk Ni(80) - Mo(20) alloy electrodes at 298 K in 0.2 M aq. NaOH and on an electrocoated Ni(80) - Mo(19) - Cd(1) electrode at 298 and 353 K. (These plots are corrected for the back reaction current near the reversible potential by the function shown).

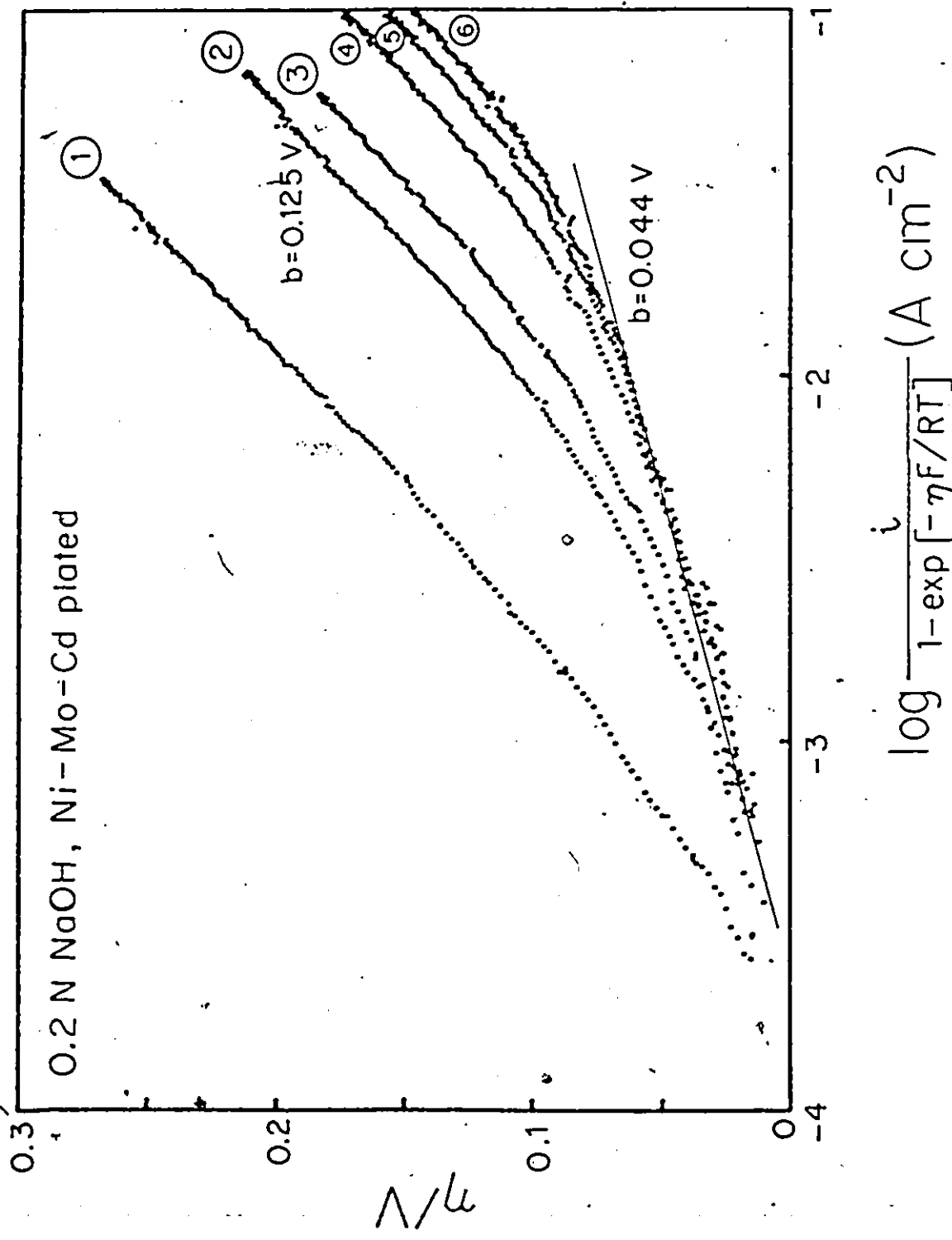


Fig. 4.1 b) Tafel plots, corrected for back reaction current, for the Ni(80) - Mo(19) - Cd(1) electrocoated electrode: 1) 274; 2) 298; 3) 308; 4) 325; 5) 338 and 6) 353K.

and/or of a change of adsorption behaviour of the H intermediate with potential. A potential for transition between one region to another is seen at $\eta = \text{ca.} - 0.075$ to -0.1 V. At Ni wire, usually a single valued Tafel slope is observed, as found previously⁶⁴, at a given temperature.

4.1.1.2 Potential Decay Behaviour

(a) Ni-Mo-Cd electrodes

The digitally acquired, potential relaxation data are shown in Figure 4.2a directly as $f(\log t)$ for four initial polarization current-densities. Figure 4.2b shows the same data plotted as $f[\log(t + \tau)]$ with the integration constant evaluated empirically (cf. eqn. 3.6 and ref. 135, 136) to give a linear relation in $\log(t + \tau)$ for short times when $\tau > t$ at the early stage of potential decay. Note that an estimate of C can also be made from τ using the definition of τ given by eqn. (3.5).

The corresponding estimated C values are listed in Tables 4.1 (Ni) and 4.2 (Ni-Mo-Cd). The surface capacitance for the Ni electrode calculated by eqn. (3.5) ($C = \tau i/b'$) from the data shown in Fig. 4.5, is a constant and small value : $51 \pm 4 \mu\text{F cm}^{-2}$, for four initial current-densities (see Table 4.1), which can be reasonably assigned to C_{dl} ($25 \mu\text{F cm}^{-2}$) if we take the ratio of real/apparent surface area as 2 (the roughness factor has been usually found to be ca. 1.5-2 for bright Pt wire electrodes by the CV method). This implies that the assumption $C_p \rightarrow 0$ applies for integration of eqn. (3.4) for the region of significant overpotentials ($>0.15\text{V}$, for Ni), i.e. in this potential region

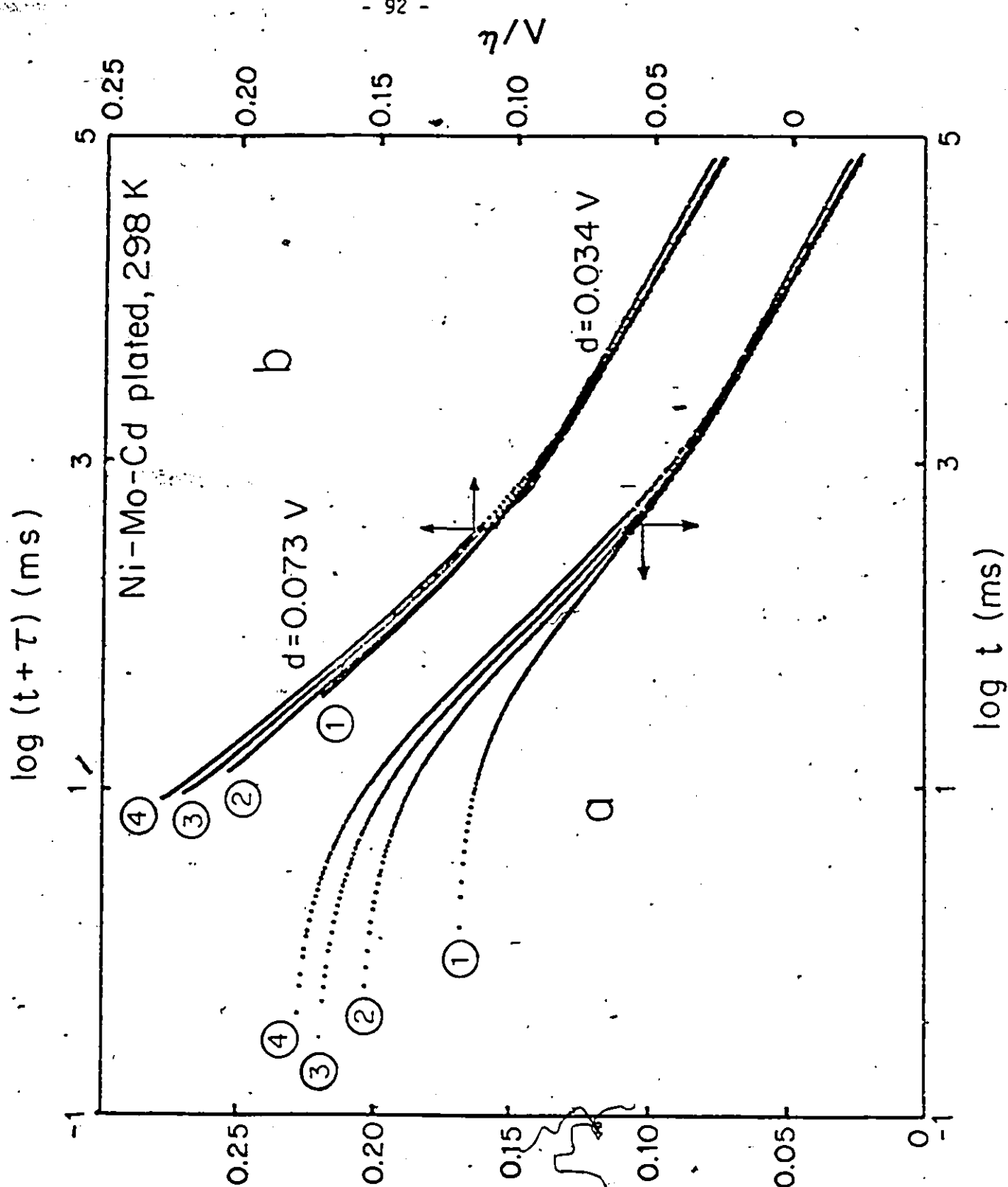


Fig. 4.2 Potential-decay plots for the HER at Ni(80)-Mo(19)-Cd(1) plated electrodes at 298K in 1.0 M aq. NaOH.

Curves (a): η vs $\log t$ plots

Curves (b): η vs $\log(t + \tau)$ plots

for interruption of polarization at 4 apparent current density values:

1) 0.10; 2) 0.15; 3) 0.20 and 4) 0.30 A cm⁻².

Table 4.1 Estimates of C from τ for Ni electrode (298K)

$$(C = \tau i / \bar{b}; \quad b = 0.12V; \quad \bar{b} = b/2.303 = 0.052V)$$

	$i (Acm^{-2})$	$\tau (s)$	$C (\mu Fcm^{-2})$	$C, average$
1	0.55×10^{-3}	4.5×10^{-3}	48.3	51 ± 4 $\mu F cm^{-2}$
2	1.45×10^{-3}	1.7×10^{-3}	48.3	
3	4.3×10^{-3}	0.5×10^{-3}	47	
4	15.3×10^{-3}	0.17×10^{-3}	55	

Table 4.2 Estimates of C from τ for Ni-Mo-Cd electrode (298K)

$$(C = \tau i / \bar{b}, \quad \bar{b} = 0.125V/2.303 = 0.054V)$$

	$i (Acm^{-2})$	$\tau (s)$	$C (\mu Fcm^{-2})$	$C (\mu Fcm^{-2})$ after taking account of roughness factor 450X
1	0.1	30×10^{-3}	55×10^3	122
2	0.15	12×10^{-3}	33×10^3	73
3	0.2	9.5×10^{-3}	35×10^3	77
4	0.3	8.0×10^{-3}	44×10^3	97

θ_H reaches a constant limit (so that $C_\phi = 0$). Then only the double layer capacitance is involved (for Ni at $\eta > 0.15V$). However, the corresponding estimated C values for Ni-Mo-Cd plated electrode in Table 4.2 are not only still appreciably greater than C_{dl} , even taking account the roughness factor which for these electrode is ca. 450x (as determined by the Kr-B.E.T. method), but the values are also not quite coincident for four initial current-densities. This can be easily understood since, in this case, $b+d$ and $C(V)$ is potential-dependent over the whole studied potential range; the integration of eqn. (3.4) is then not valid if $C(V)$ is not a constant. This also suggests that electrode pre-history determines, in part, the potential-decay behaviour, e.g. due to some sorption of H as Ni hydride (cf. ref. 147).

Figure 4.3 shows plots of η vs $\log(-d\eta/dt)$ at 298 K for the data processed according to equation (3.2). In contrast to the η vs $\log t$ plots shown in Fig. 4.1a, the plots of η against $\log(-d\eta/dt)$ are coincident in the cases of curves 3, 4, 5 and 6 of Fig. 4.3 at their upper ends where $\eta > 0.1V$; in these plots it is to be noted that there is no arbitrariness involved, as there is unavoidably in plots such as those in Fig. 4.2b due to empirical evaluation of τ . This difficulty is avoided by treating the data according to equations (3.13) or (3.14).

We see from Fig. 4.3 that the η vs $\log(-d\eta/dt)$ plots also exhibit two principal linear regions having different slopes like the Tafel relations shown in Figure 2, to which they correspond.

Fig. 4.4 shows similar plots for $i = 0.15$ or 0.20 A apparent cm^{-2} for four temperatures. Like the Tafel plots of Fig. 4.1,

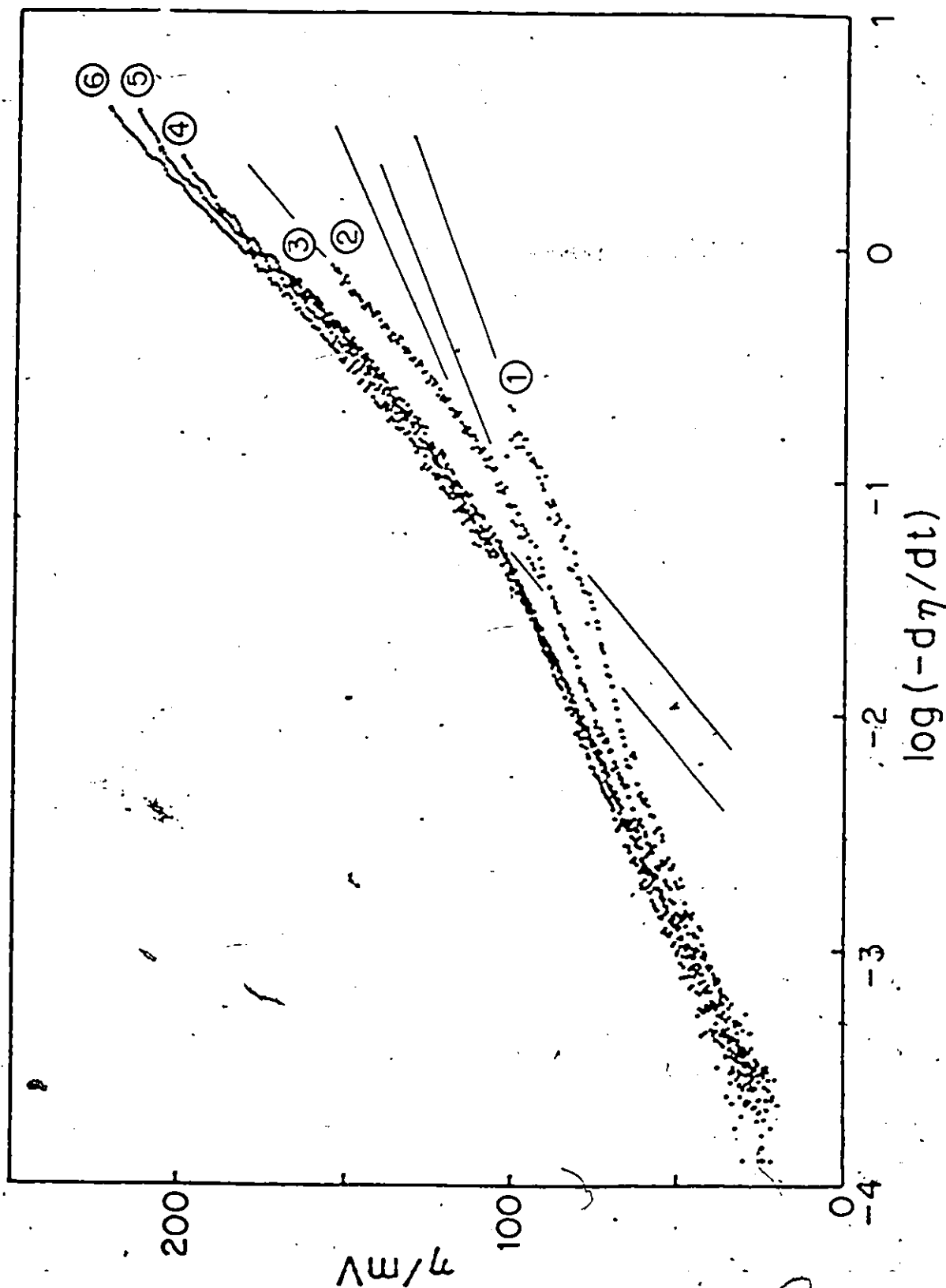


Fig. 4.3 Plots of η vs $\log(-dn/dt)$ for the h.e.r. at Ni(80)-Mo(19)-Cd(1) plated electrodes for six initial apparent current densities: 1) 0.020; 2) 0.060; 3) 0.10; 4) 0.15; 5) 0.20 and 6) 0.30 A cm⁻²; T = 298K.

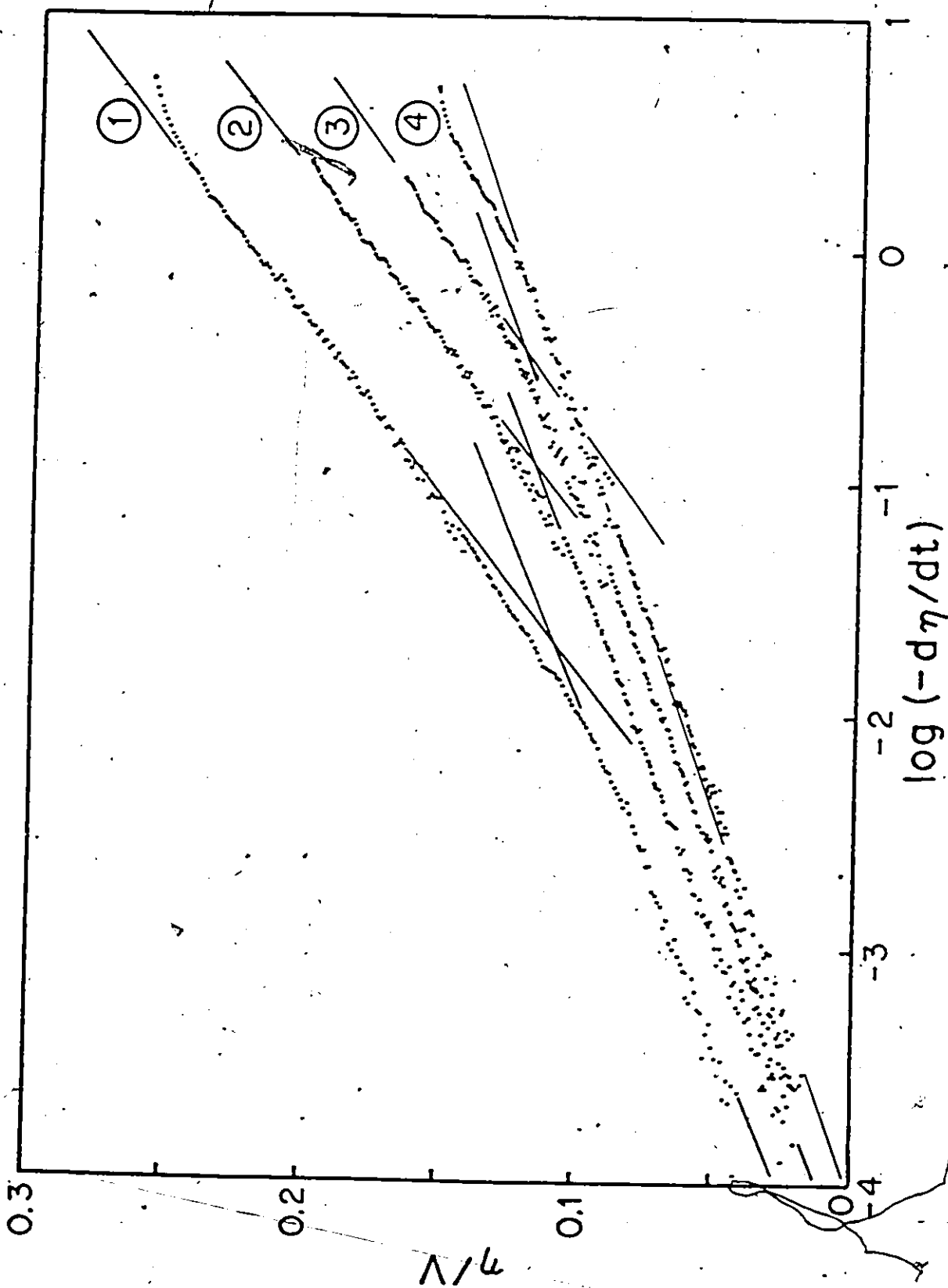


Fig. 4.4 As in Fig. 4.3 but for four temperatures: 1) 278K (0.15 A cm^{-2}); 2) 298K (0.15 A cm^{-2}); 3) 319K (0.20 A cm^{-2}) and 4) 341K (0.30 A cm^{-2}).

there is evidently a progressive change of the H electro sorption behaviour with temperature: the lower slope region (30 mV) becomes progressively extended as temperature is increased to 341 K.

(b) Ni wire electrodes

At Ni wire electrodes, two regions of the decay kinetics are again observed (Fig. 4.5a) but the Tafel plot (Fig. 4.1) is a single line as is usually found. The corresponding η vs $\log(t + \tau)$ plots for Ni wire are shown in Fig. 4.5b for four initial i 's, while Fig. 4.6 shows the corresponding η vs $\log(-dn/dt)$ plots, giving the capacitance behaviour (eqn. 3.14). As with the Ni-Mo-Cd electrodes, two regions of the $\log(-dn/dt)$ behaviour are observed, corresponding respectively to the 118 and 61 mV slopes in this figure. Also, with the Ni wire electrode, the populations of points corresponding to the potential decays become almost coincident for the four initial i 's when $t \gg \tau$. This means that the decay behaviour itself in $\log(t + \tau)$ must, in this case, also be almost coincident, as is in fact seen from Fig. 4.5b. The empirical constant τ and the corresponding C at initial overpotentials are listed in Table 4.1.

4.1.1.3 Pseudocapacitance Behaviour of o.p.d H at Ni Wire and Ni-Mo-Cd Coated Electrodes.

(i) C_ϕ for adsorbed H as $f(\eta)$

From the plots of $\log(-dn/dt)$ vs η , it is possible to calculate the derivative $d \log C/d\eta$ using equation (3.12). Since, experimentally, $\log(-dn/dt)$ appears limitingly linear,

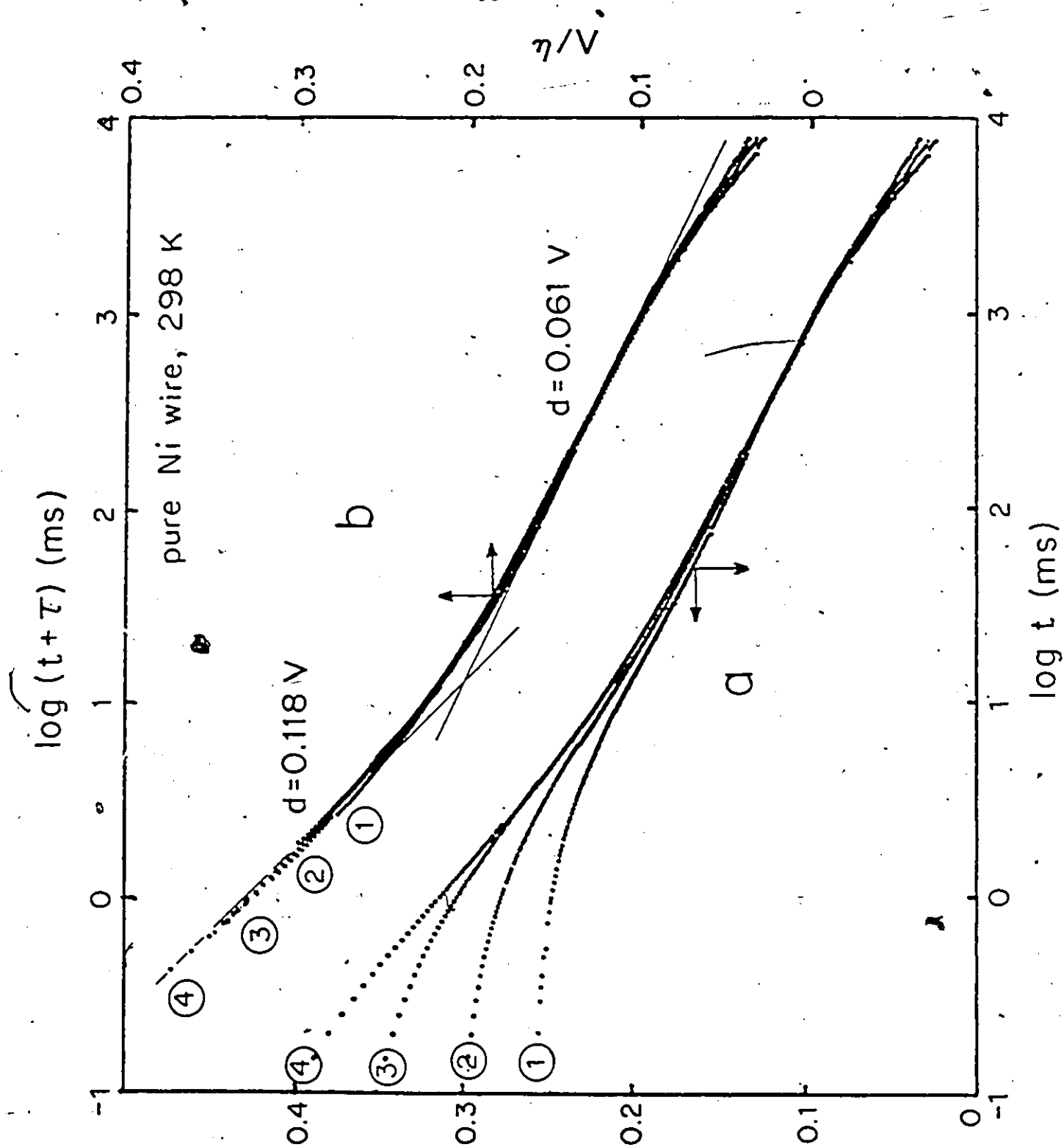


Fig. 4.45 Potential-decay plots for the HER at pure Ni wire electrodes at 298K in 0.2 M aq. NaOH.

Curves (a): η vs $\log t$ plots

Curves (b): η vs $\log(t + \tau)$ plots

after interruption of polarization at 4 current densities: 1) 0.55×10^{-3} ; 2) 1.45×10^{-3} ; 3) 4.3×10^{-3} and 4) $15.3 \times 10^{-3} \text{ A cm}^{-2}$.

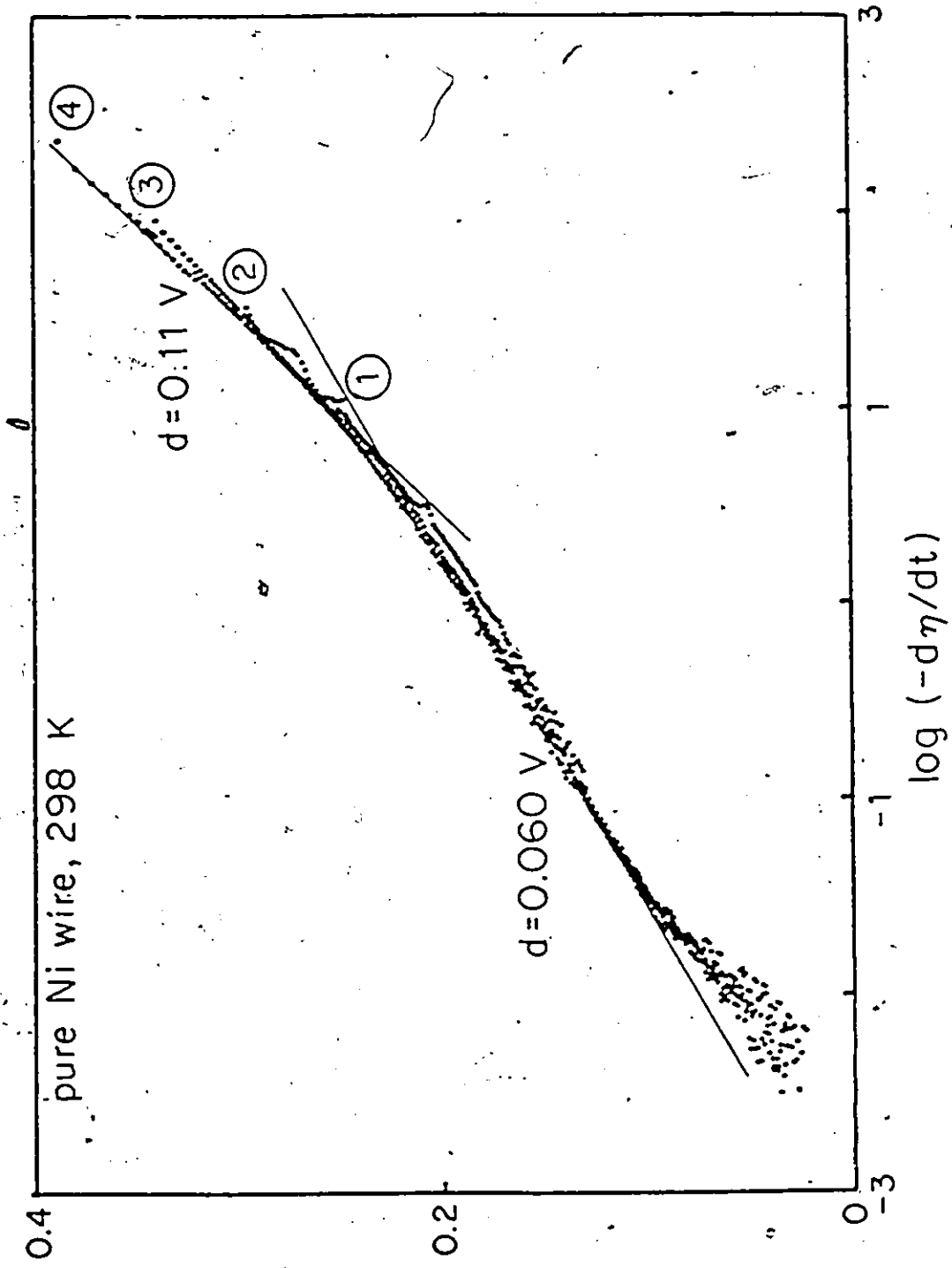


Fig. 4.6 Plots of η vs $\log(-dn/dt)$ for the h.r.e. at pure Ni wire electrodes at 4 initial current densities (as in Fig. 4.5): 1) 0.55×10^{-3} ; 2) 1.45×10^{-3} ; 3) 4.3×10^{-3} and 4) $15.3 \times 10^{-3} \text{ A cm}^{-2}$ at 298K; 0.2 M aq. NaOH.

in η over two regions, $d \log C/d\eta$ is obtained simply as the sum of, minus the reciprocal slope, d^{-1} , of those linear regions and the Lefat slope, b^{-1} (see eqn. 3.15). Results are given in

Table 4.3:

TABLE 4.3 Values of $d \log C\phi/d\eta$ for the
Two Linear Regions of the Plots in Fig. 4.3 and 4.6 (T=298K)

Electrode	b(upper)	b(lower)	d(upper)	d(lower)	$d \log C\phi/d\eta$
Ni wire	0.12	0.12	0.118	0.061	η 0 (upper) -8.0(lower)
Ni-Mo-Cd	0.125	0.044	0.065	0.030	-7.4(upper)-10.6(lower)

Since $d \log C\phi/d\eta$ is approximately constant over an appreciable range of potential, $C\phi$ is evidently almost an exponential function of η over that range. This is illustrated in Fig. 4.9, to be discussed below, where the $\log C$ vs η plots are shown for the three types of electrode materials. However, the results in Table 4.3 also show that the arguments of the exponents are not simply $\eta F/RT$ but are rather arbitrary numbers.

We now show how a more complete evaluation of the capacitance behaviour can be made directly with eqn. 3.2a in the forms 3.13 or 3.14, using the η vs $\log i$ and the $\eta(t)$ behaviour differentiated to give dn/dt . Figure 4.7 shows C as $f(\eta)$ at Ni wire at 276, 298 and 318 K while Fig. 4.8 shows similar plots for a Ni-Mo-Cd electrode at 274, 296 and 353 K. Figure 4.9 shows the $\log C$ vs η plots for the three electrode materials for conditions defined on

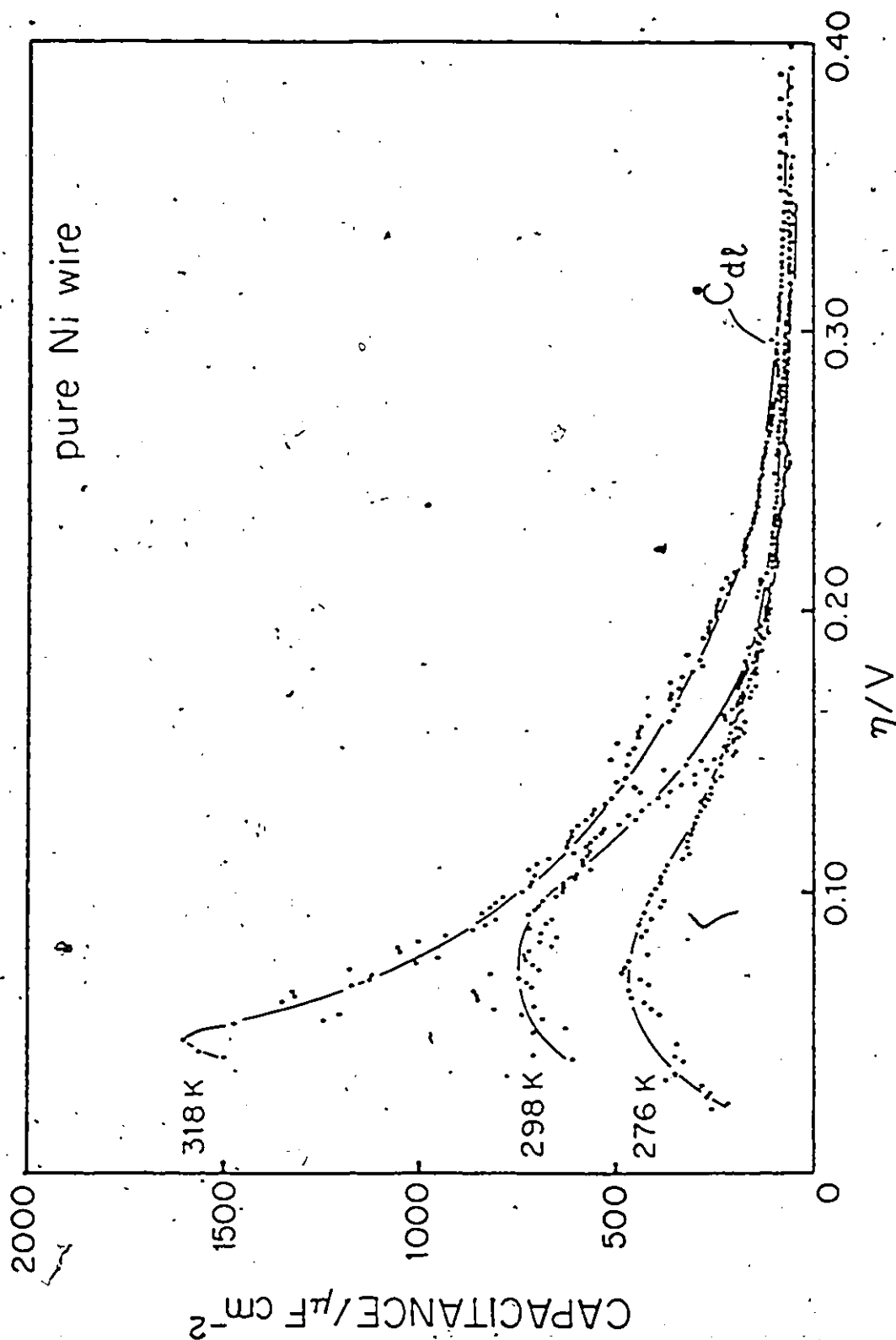


Fig. 4.7 Capacitance C vs overpotential η for the h.e.r. at pure Ni wire at 3 temperatures: 276K, 298K and 318K; 0.2 N aq. NaOH.

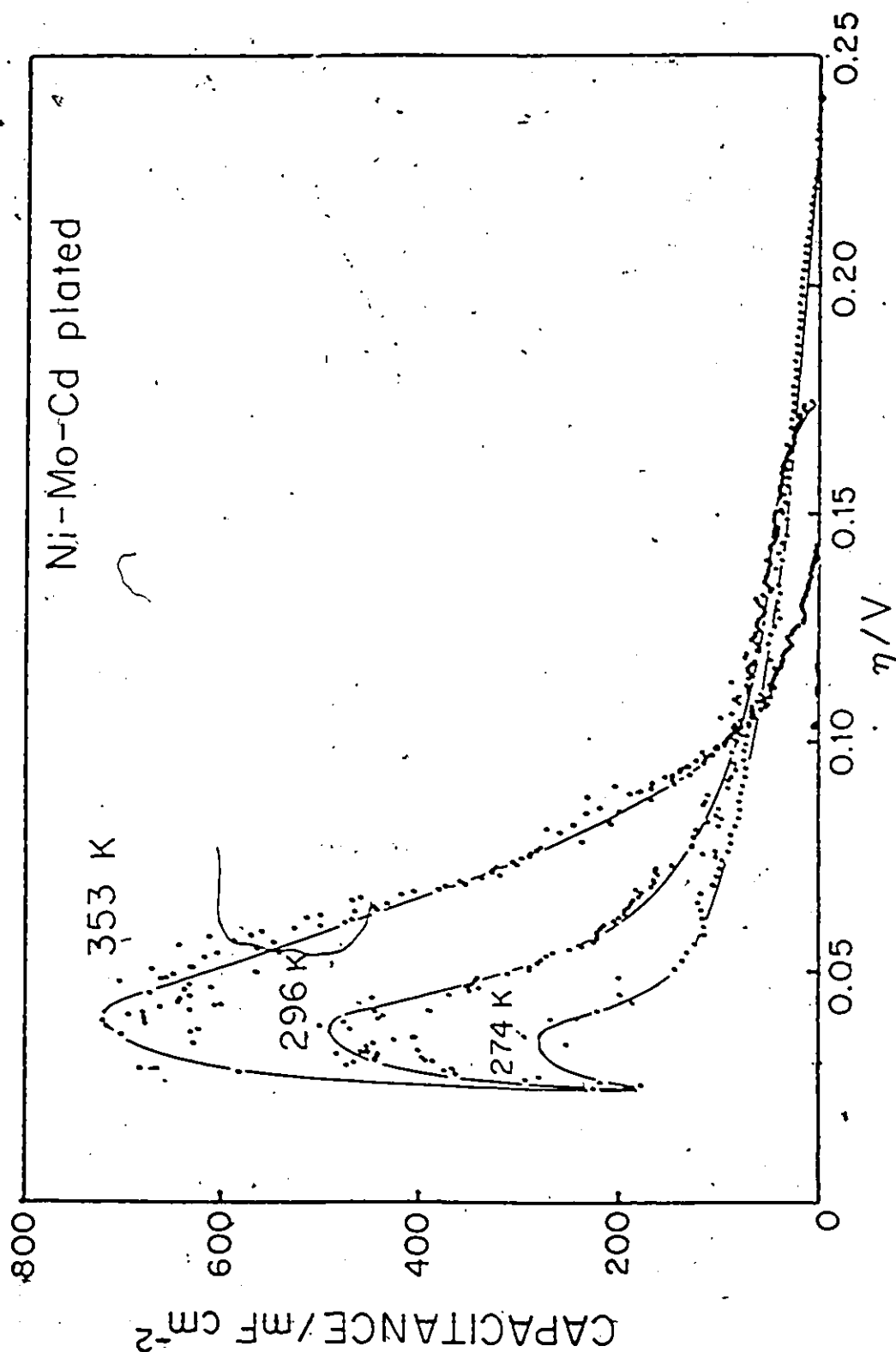


Fig. 4.8 Capacitance C vs overpotential η for the h.c.r. of the Ni(80)-Mo(19)-Cd(1) plated electrodes at 3 temperatures: 274K; 296K and 353K, 0.2 M aq. NaOH.

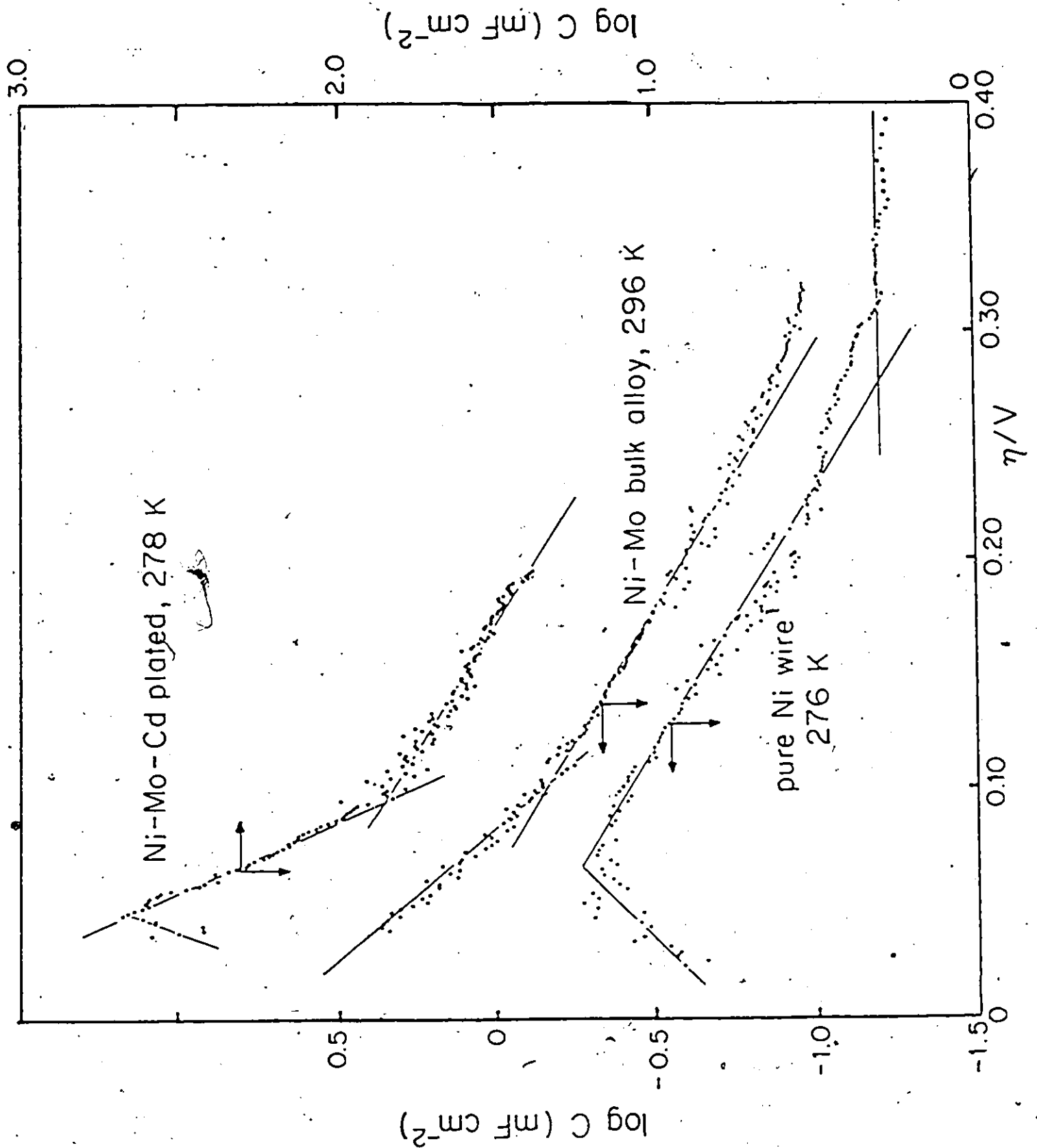


Fig. 4.9 log C vs overpotential η plots for the three types of electrode materials.

that figure. In these plots C ($-C_{dl} + C_\phi$) or $\log C$ have been calculated by means of eqns. (3.13) or (3.14), respectively, using the dn/dt values and the experimental $i(\eta)$ values over the whole range of the decay experiments. Evidently, from Figs. 4.7 and 4.8 there is a continuous variation of C_ϕ with η , exhibiting a maximum, as in fact is expected theoretically^{37-39,163}.

However, in the log plots of C in Fig. 4.9 it appears that the ascending regions of these plots exhibit two slopes corresponding possibly to two populations of the H intermediate being involved in the h.e.r. at Ni-based electrodes, (see detailed discussion in the section 4.1.2.2 on a.c. impedance work), depending on η and corresponding i values, having experimentally distinguishable exp dependences on potential.

For η more negative than ca. 0.15 to 0.25 V, C tends to reach a constant value (Fig. 4.7 - larger scale plots show this more clearly) which we presume is the double-layer capacitance for the electrodes under the prevailing experimental conditions. However, at smaller η , C rapidly increases and maxima are clearly seen for Ni wire (Fig. 4.7) and for the Ni-Mo-Cd electrode (Fig. 4.8). Since C increases in the direction of decreasing negative potential and the adsorbed H is deposited in a cathodic reaction, the constant C above cathodic overpotentials of ca. 0.15 ~ 0.25 V must correspond to the double-layer capacitance at a surface fully or partially covered by H (see below). The values of this limiting double-layer capacitance are ca. 60 μF apparent cm^{-2} for Ni wire. These values are close to the value calculated from τ in Table 4.1. Similar values are found for C_{dl} .

at the Ni-Mo-Cd electrode allowing for the real/apparent area factor of 450-X measured by the Kr BET desorption experiment referred to earlier.

From the potential-dependence of $C - C_{dl}$, we can calculate the coverage of the "overpotential-deposited" H as $f(\eta)$, to be shown in Fig. 4.11 (see below).

(ii) Possible surface oxidation process

Before proceeding further, the possibility must be recognized that, at the electrodes studied, on decline of potential towards the reversible potential for the h.e.r., a corrosion process could set in, producing a surface oxide film: $Ni + 2H_2O \rightarrow Ni(OH)_2 + H_2$. It is conceivable that formation of such a film could give rise to the observed C_ϕ behavior near the reversible potential. We consider this possibility in the light of the following information and experiments.

First, in terms of the Pourbaix diagram¹⁶⁴ for Ni in alkaline solution, oxidation can begin only at a small positive potential, ca. 0.1 ~ 0.15 V, relative to the H_2 reversible potential. Secondly, cyclic voltammograms (Fig. 4.10) for both Ni and the Ni-Mo-Cd electrodes show that surface oxidation processes do not commence until potentials are attained that are significantly more positive than those corresponding to the range of potentials where C_ϕ is appreciable (Figs. 4.7-9). The onset of surface oxidation occurs, in fact, at potentials somewhat more positive than thermodynamically expected¹⁶⁵ owing to irreversibility in the process, familiar in oxide film formation^{78,100}. Also the

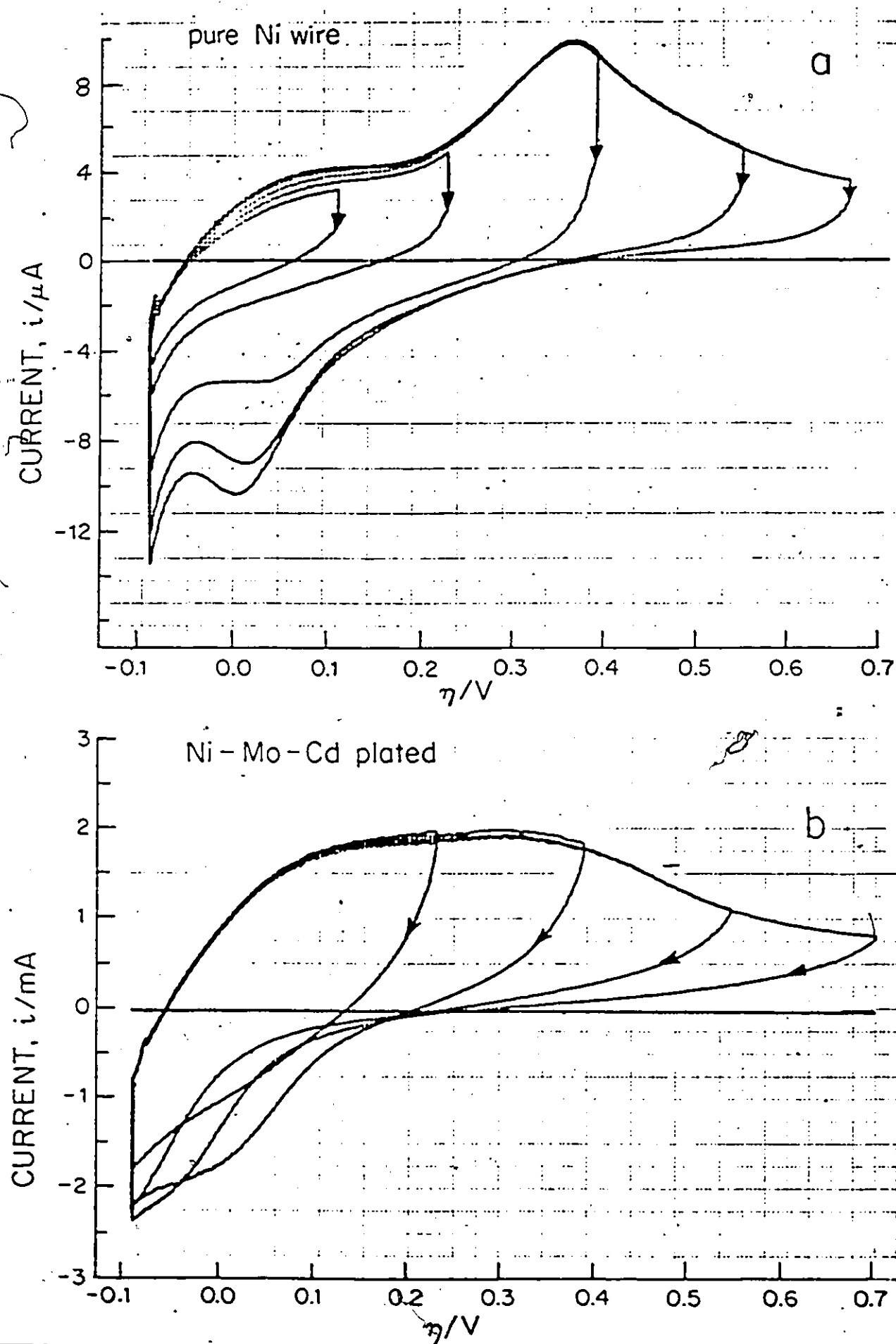


Fig. 4.10 Cyclic-voltammetry i vs η profiles over various potential ranges for a) pure Ni wire;

b) Ni(80)-Mo(19)-Cd(1) plated electrode in 0.2 N aq. NaOH. $T = 298K$. Sweep-rate 18.9

$mV s^{-1}$. N_2 bubbled. Before each cycle, potential was held at $\eta = -0.09 V$ for 180 s.

formation charge involved is >> that corresponding to integration of the C_ϕ vs η profiles derived here for Ni.

4.1.1.4 H coverage

From the potential decay behavior, information on H coverage is revealed through the pseudocapacitance $C_\phi = q_1 d\theta_H / d\eta$. θ_H or change of θ_H with η can be evaluated by integrating the experimentally determined relation between C_ϕ and η . The adsorption isotherm and the corresponding C_ϕ for various conditions were discussed in section 1.5.2 (see eqn. (1.11) and (1.13)).

The observed potential ranges of appreciable H pseudocapacitance are -0.02 to -0.3V E_H at Ni wire (278, 298 K) and -0.01 to -0.25 V E_H at the Ni-Mo-Cd composite electrodes (319 K). The corresponding fractional coverages by H, or changes in coverage, are evaluated by integrating $C_\phi(\eta)/q_1$ with respect to η , giving θ_H as $f(\eta)$ as shown in Fig. 4.11.

The H deposition charges corresponding to the above potential ranges at 298K are $75.6 \pm 5 \mu\text{C cm}^{-2}$ and $22.8 \pm 2 \text{mC cm}^{-2}$, respectively, and are temperature dependent. These figures are substantially less than corresponds to a monolayer of H, ca. $257 \mu\text{C cm}^{-2}$ for the (111) plane at Ni or $210 \mu\text{C cm}^{-2}$ for Pt¹⁰⁰, allowing for a real/apparent area of ca. 220 X at the electrocoated material and ca. 2X at Ni wire. These data suggest that a steady-state coverage by H less than a monolayer arises at the Ni or Ni-Mo-Cd electrodes as overpotential increases. This, as well as the observed Tafel slopes, shows that recombination of chemisorbed H cannot be the rate-controlling step in the h.e.r. at the Ni electrode surface.

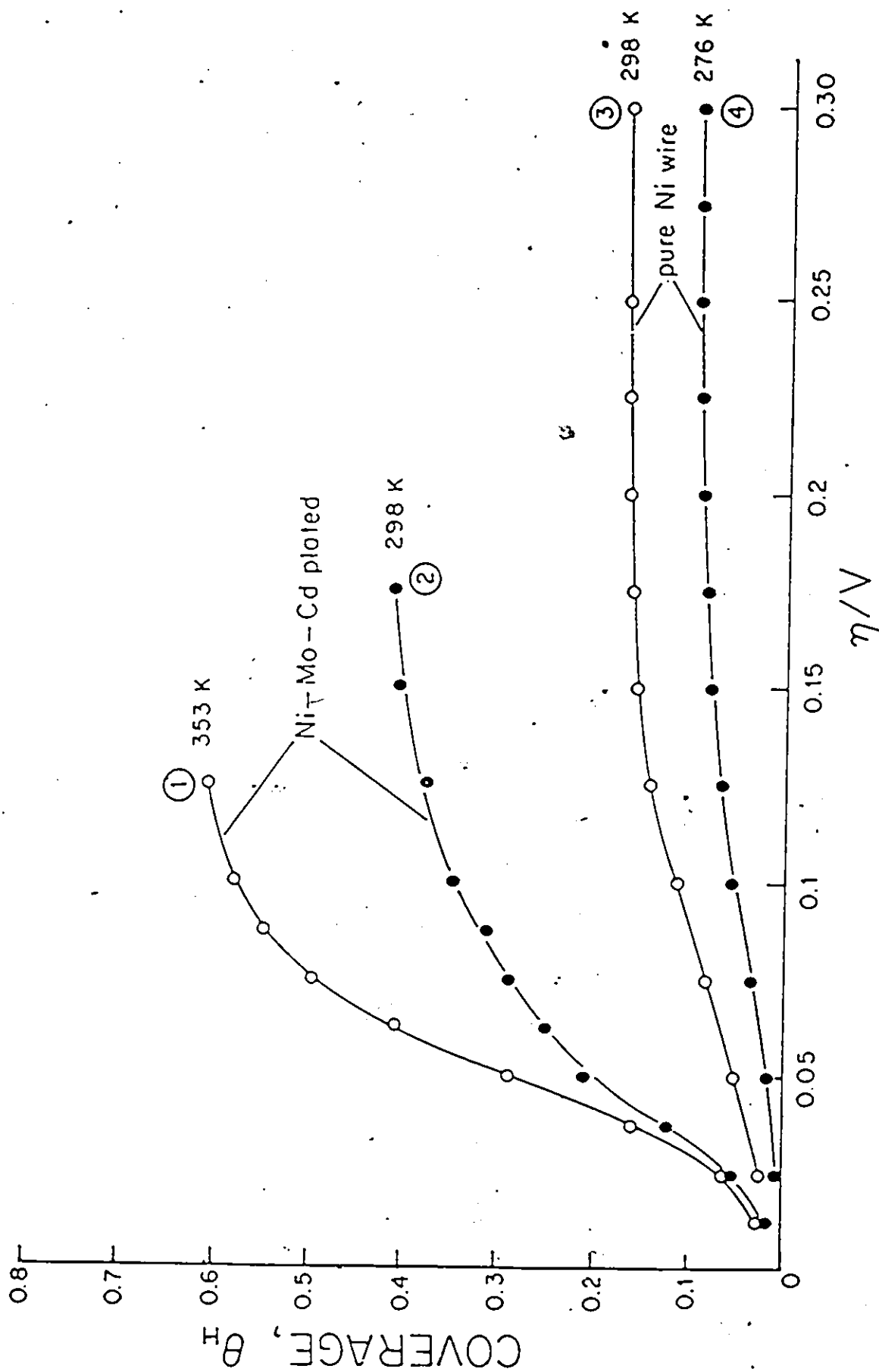
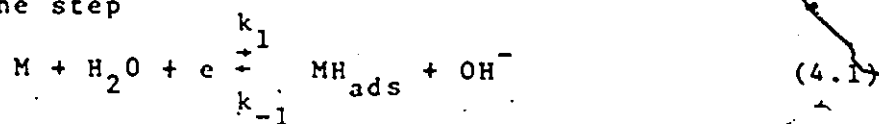


Fig. 4.11 Coverage of H (θ) vs overpotential η for the h.e.r. at Ni(80)-Mo(19)-Cd(1) plated electrodes at 1) 353K; 2) 298K and at pure Ni wire electrodes at 298K and 276K. Coverage

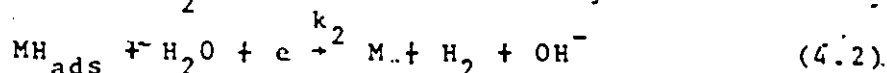
θ , derived from the C data shown in Figs. 4.7 and 4.8 assuming real/apparent area ratio

is ca. 220 for the composite electrodes and ca. 2 for Ni wire taking $\theta_H = 1$ corresponding

In the case of the step



coupled with H desorption and H₂ molecule formation by



we can show, as follows, that limiting steady-state H coverages < 1 are expected. The relevant rate equations for processes (4.1) and (4.2) are:

$$v_I = k_1 (1 - \theta_H) \exp\{\beta \eta F/RT\} \equiv l(1 - \theta_H) \text{ say}; \quad (4.3)$$

$$v_{-1} = k_{-1} \theta_H c_{OH^-} \exp\{-(1 - \beta)\eta F/RT\} \equiv m\theta_H \text{ say}; \quad (4.4)$$

and

$$v_2 = k_2 \theta_H \exp\{\gamma \eta F/RT\} \equiv n\theta_H \text{ say} \quad (4.5)$$

where β and γ are symmetry factors for charge transfer, and l , m and n are defined obviously according to the relations (4.3), (4.4) and (4.5). The steady-state condition for H coverage is then

$$d\theta_H/dt = 0 = v_I - v_{-1} - v_2 \quad (4.6)$$

i.e.

$$l(1 - \theta_H) - m\theta_H - n\theta_H = 0 \quad (4.7)$$

or

$$\theta_H = l/(l + m + n) \quad (4.8)$$

noting that l , m and n are exponential functions of η as in (4.3), (4.4) and (4.5). Corresponding to equation (4.8), the pseudocapacitance $q_1 d\theta_H/d\eta$ is

$$C_\phi = \frac{Fq_1}{RT} \cdot \frac{l m}{(l + m + n)^2} \quad (4.9)$$

taking $\beta = \gamma = 0.5$.

Inserting the potential-dependent factors,

$$\theta_H = 1 / (1 + K_1^{-1} c_{OH^-} \exp\{\eta F/RT\} + k_2/k_1) \quad (4.10)$$

At appreciable cathodic overpotentials*, it is seen that θ_H reaches limiting values for the mechanism 4.1, 4.2 given by

$$\theta_{H,lim} = 1 / (1 + k_2/k_1) \quad (4.11)$$

i.e., θ_H is determined by the extent to which the discharge step, producing chemisorbed H, and the reverse are in "equilibrium"[†], thus, for $k_2 \ll k_1$, $\theta_H \rightarrow 1$ limitingly and step 1, -1 is almost in complete equilibrium. Alternately, when $k_2/k_1 > 1$, i.e. when the h.e.r is "discharge-controlled", there is a varying degree of quasi-equilibrium in step (4.1) and, with increasing overpotential, limiting fractional coverages by H, θ_H , less than 1, can arise as shown in Fig. 4.12 (curves a). The limiting values of θ_H as a function of k_2/k_1 are shown in Fig. 4.13. The corresponding C_ϕ maxima are then smaller (Fig. 4.12 curves b) than for the quasi-equilibrium case^{104,105}. We note that as k_2/k_1 goes from $\ll 1$ to $\gg 1$ the kinetics of the pathway 4.1, 4.2 change, respectively, from being "desorption-controlled" (through 4.2) to being "discharge-controlled" (through 4.1) with θ_H then $\ll 1$.

This rather special feature of the behaviour of the dual reaction sequence 4.1, 4.2 arises because both the desorption and the adsorption (discharge) steps have the same dependence on potential, if $\beta = \gamma$, and is a diagnostic aspect of this mechanism.

Since we have assumed an exponential dependence of K on θ_H

*At low overpotentials, θ_H is influenced by K_1^{-1} and by η , so that the general eqn. (4.10) must be used for evaluation of θ_H as $f(\eta)$ under such conditions.

[†]When this is the case, the C_ϕ differs somewhat¹⁶³ from its "reversible" value given by eqn. (1.13)

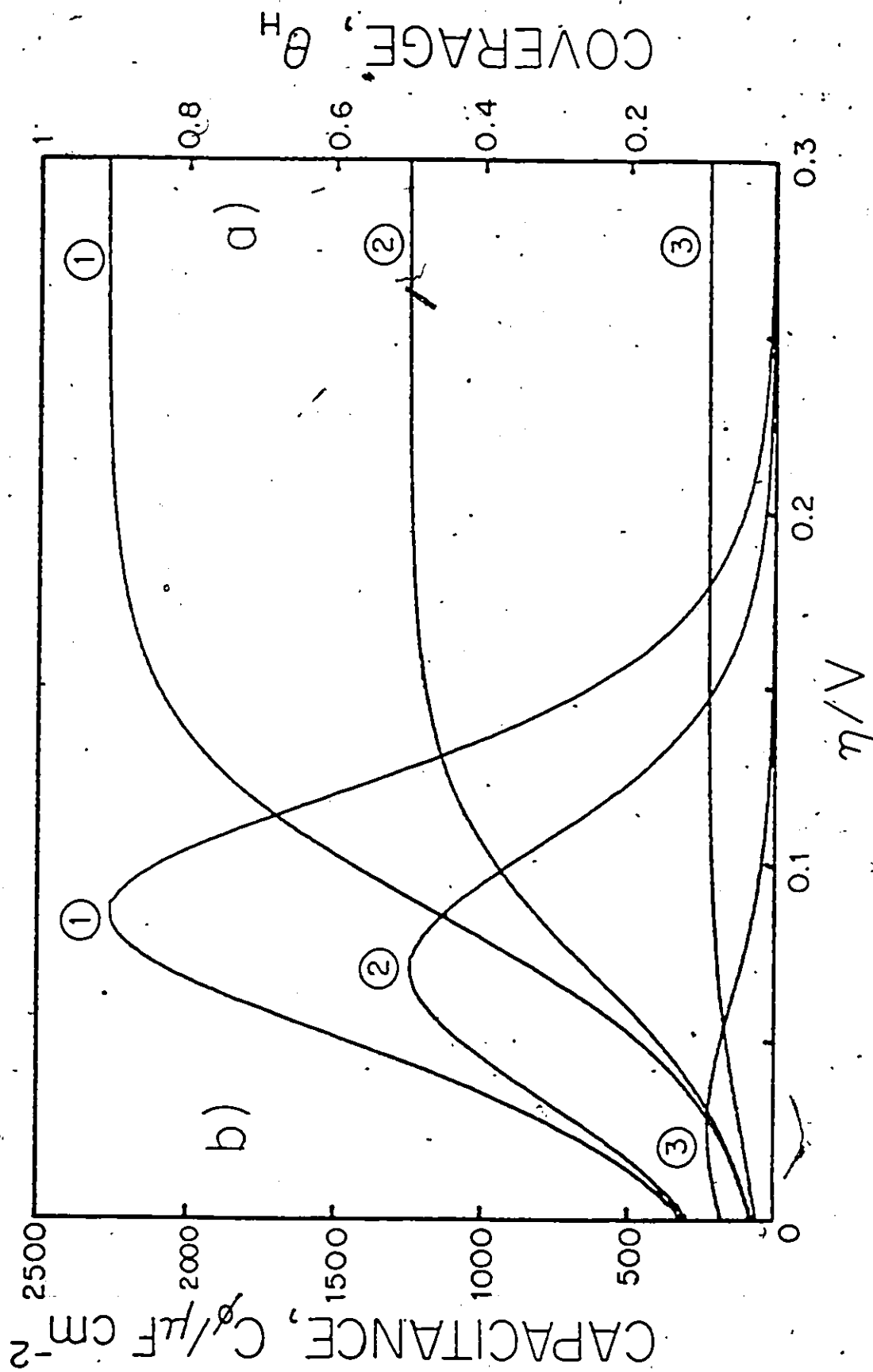


Fig. 4.12 Calculated plots of a) θ_H vs overpotential for 3 k_2/k_1 values, using eqn. (4.8); b) C_ϕ vs overpotential using eqn. (4.9), taking $c_{OH^-} = 1$, $q_1 = 257 \mu C \text{ cm}^{-2}$, $T = 298K$, $k_1 = 1$, $k_{-1} = 30$ with 1) $k_2 = 0.1$; 2) $k_2 = 1$; 3) $k_2 = 10$ (arbitrary units for k 's since only ratios are involved).

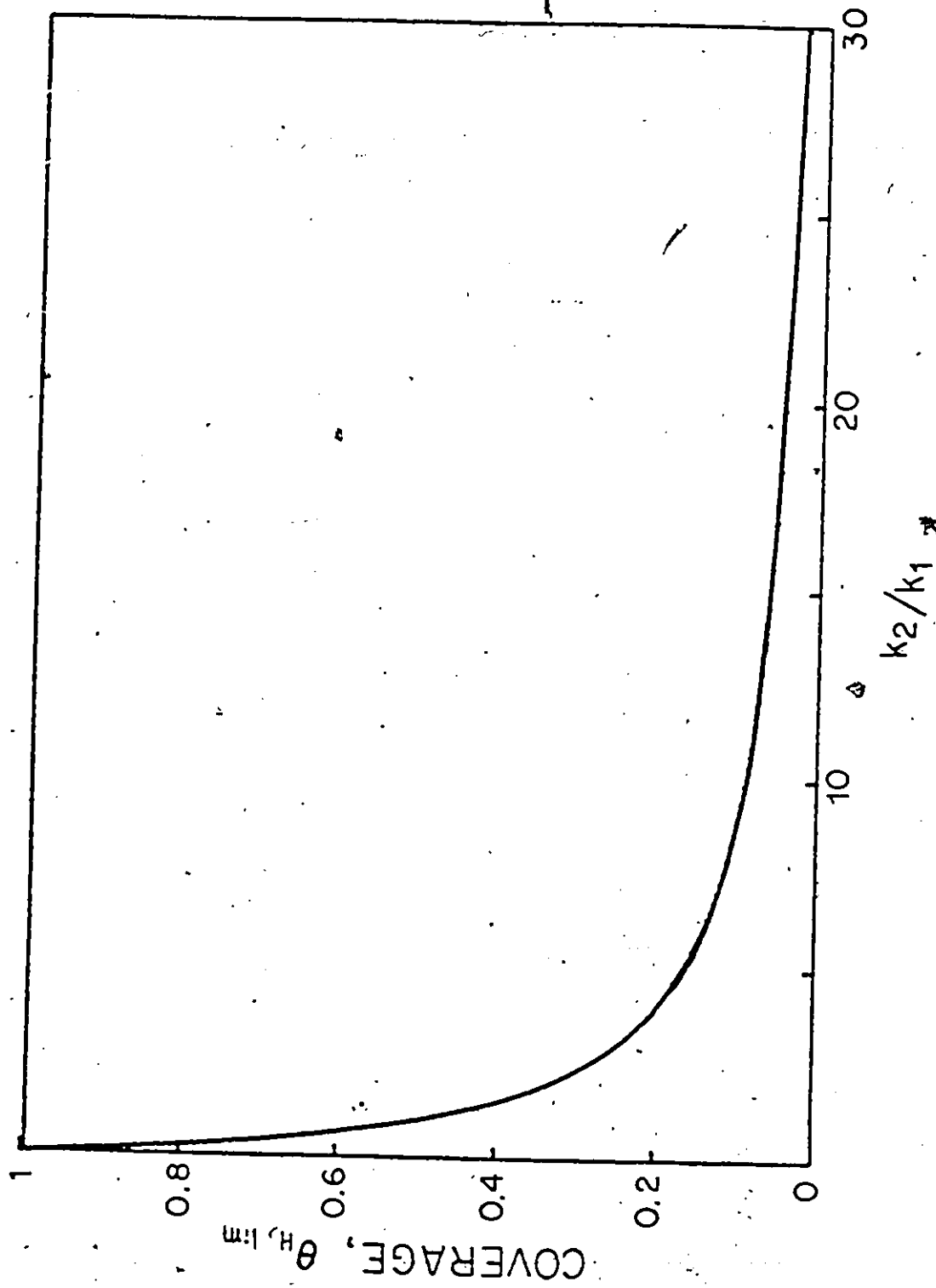


Fig. 4.13 Calculated plots of limiting coverage $\theta_{H,lim}$ for mechanism 4.1, 4.2 vs k_2/k_1 , using eqn. (4.11).

(eqn. 1.9), we may reasonably extend this assumption of exponential dependence of θ_H to the rate constants k_1 , k_{-1} and k_2 as well³⁷⁻⁴⁰. It is clear then that the rate of the adsorption step will decrease while that of the desorption step will increase with θ_H .

In the general case, corresponding to eqn. (1.11) where effects of significant interactions are included, the steady-state condition gives

$$\frac{1-\theta_H}{\theta_H} \exp[-g\theta_H] = k_2/k_1 + k_1^{-1} \exp[-\eta F/RT] \quad (4.12)$$

θ_H then has limiting values at appreciable cathodic overpotentials dependent on g as well as the rate constant ratio k_2/k_1 . Correspondingly, the H pseudocapacitance also depends on these two parameters, which can only be explicitly evaluated numerically, and is given by

$$C_\phi = \frac{Fq_1}{RT} \frac{k_1^{-1} \exp(-\eta F/RT)}{\exp(-g\theta_H) \{ (g\theta_H + 1)/\theta_H^2 - g \}} \quad (4.13)$$

As may be expected, for $g > 0$, a much wider spread of values of the ratio k_2/k_1 is required* to cause $\theta_{H,2}$ to vary from 1 to small values than is the case for Langmuir adsorption ($g=0$)^{38,39,146}. This can be seen in Fig. 4.14 a and b which show the relations between C_ϕ and η (calculated from eqn. 4.13), and θ_H and η (calculated from eqn. 4.12), based on two assumed ratios of k_2 to k_1 : in Fig. 4.14a, with $k_2/k_1 = 10^{-3}$, i.e. near equilibrium in the discharge step and in Fig. 4.14b with $k_2/k_1 = 10^{-1}$, i.e. for the steady-state situation. Both sets of cases are evaluated for $g = 0, 2$ and 5 .

*In the case where g may be significantly > 0 , it follows from eqn. (4.12) that the ratio k_2/k_1 required for a given value of $\theta_{H,lim}$ to be attained is smaller.

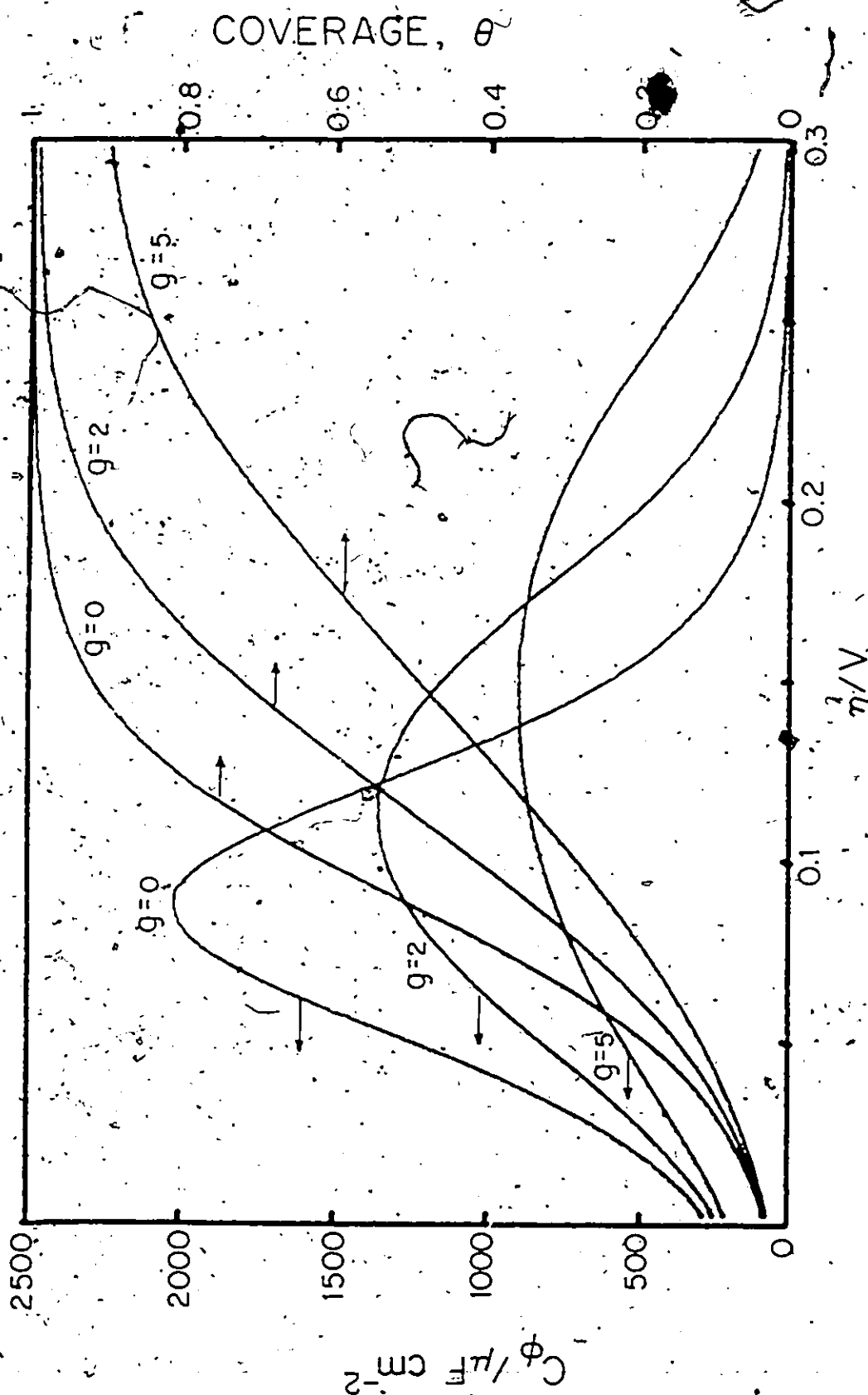


Fig. 4.14(a) Calculated plots of θ_H and C_ϕ vs η , using eqns. (4.12) and (4.13) respectively, with $k_2/k_1 = 10^{-3}$ and $K_1 = 0.1$ for three g values: $g=0$, 2 and 5 (the cases for step 4.1 in quasi-equilibrium).

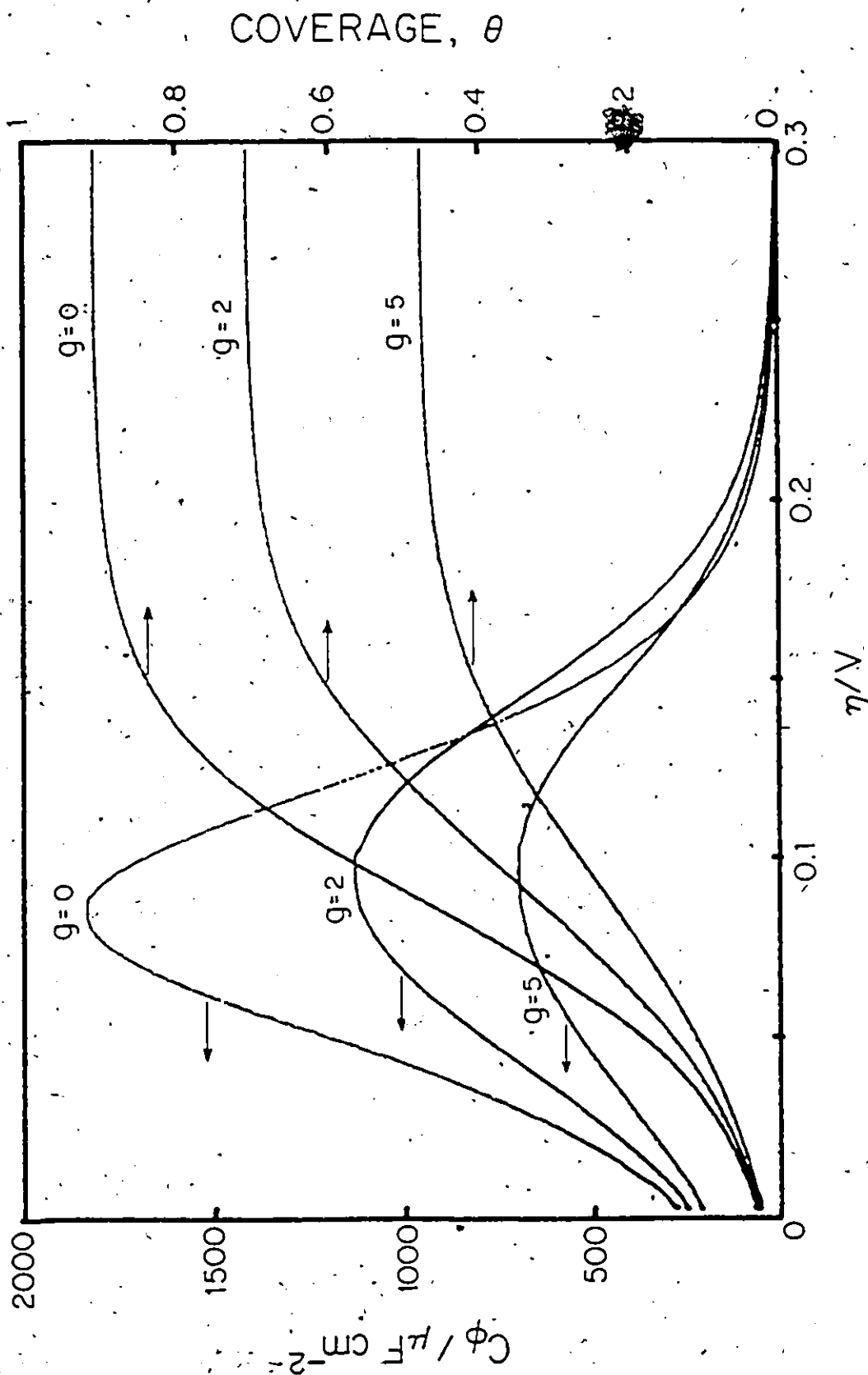


Fig. 4.14(b) Calculated plots of θ_H and C_ϕ vs η , using eqns. (4.12) and (4.13) respectively, with $k_2/k_1 = 0.1$ and $K_1' = 0.033$ for three g values: $g=0$, 2 and 5 (the cases for which rate constants for step 4.1 and 4.2 are comparable, i.e., step 4.1 is not in quasi-equilibrium). Notice that in this case the behaviour of C_ϕ and θ_H vs η is different from that in.

4.1.1.5 Relation to the Experimental Behaviour

It is clear that the experimental coverage and H pseudo-capacitance behaviour shown in Figs. 4.7 and 4.8, which corresponds to attainment of a limiting coverage θ_H substantially < 1 at both types of electrode, is rationalized by the above treatment of reaction scheme 4.1, 4.2 in the steady-state.

From the experimental data, we see from Fig. 4.11 that k_2/k_1 calculated from $\theta_{H,lim}$ using eqn. 4.11 (Langmuir case) would be 4.7 for Ni wire and ca. 1.4 for the Ni-Mo-Cd composite electrode material at $T = 298K$. These results also show that it is not correct to assume, as has often been done previously, that when the proton-discharge, H adsorption step 4.1 is rate-controlling, the H coverage is very small. Evidently, at the various Ni based electrodes studied here, the rate constants of the "discharge" and "desorption" steps are rather comparable so that it is not possible to define unambiguously the "rate-controlling" step for the behaviour actually observed here.

From the present results at Ni and Ni-Mo-Cd, we can conclude that, with increasing η , the h.e.r at these metals proceeds on a surface incompletely but still appreciably covered by H, the limiting fractional coverage being determined in the steady-state by the ratio of the rate constants of the H discharge and the desorption steps. Integration of the observable C_ϕ vs η profiles gives experimentally determined values for these limiting coverages and hence the ratio of the rate constants. We see from Fig. 4.11 and from Figs. 4.7 and 4.8 that the limiting coverages by H are

quite temperature dependent. This is easily rationalized in terms of the above treatment since $\theta_{H,lim}$, being determined by the ratio k_2/k_1 , will normally be temperature dependent since k_2 and k_1 will be expected to be associated with different activation energies.

For the mechanism involving the reaction steps 4.1, 4.2 it is expected that b will remain constant with a value ca. 0.12 V when θ_H is near 1 or is otherwise constant. In the Langmuir case (eqn. 1.11, $g = 0$), b will in fact remain constant down to ca. -50 mV from the standard potential ($\theta_H = 0.5$) for H adsorption through step 4.1. Below this potential, θ_H will start to decrease in a potential-dependent manner and the Tafel slope will become less. Correspondingly, C_ϕ increases approximately exponentially with $-\eta F/RT$ as $|\eta|$ decreases (Fig. 4.9). Thus we see that the slopes of the η vs $\log(t + \tau)$ and η vs $\log(-d\eta/dt)$ plots in relation to $d\eta/d \log i$ are consistent and correspond to the h.e.r. proceeding with a limiting constant θ_H at a high η and a potential-dependent θ_H at $\eta < \text{ca. } 0.15V$ for the Ni and the Ni-Mo-Cd electrodes.

Simulated Tafel plots were calculated for the mechanism 4.1, 4.2 for 3 values of k_2/k_1 with step 4.2 or step 4.1 rate-controlling. The results are shown in Fig. 4.15. A transition from almost single slope behaviour ($b = 0.118 V$) to two-slope behaviour ($b = 0.044$ to $0.118 V$) arises as k_2/k_1 is decreased from 10 to 0.1 corresponding to the calculated coverage vs potential relation of Fig. 4.12. This change of slope behaviour corresponds, of course, to a change of rate-controlling step and to the different coverage conditions that obtain as k_2/k_1 varies.

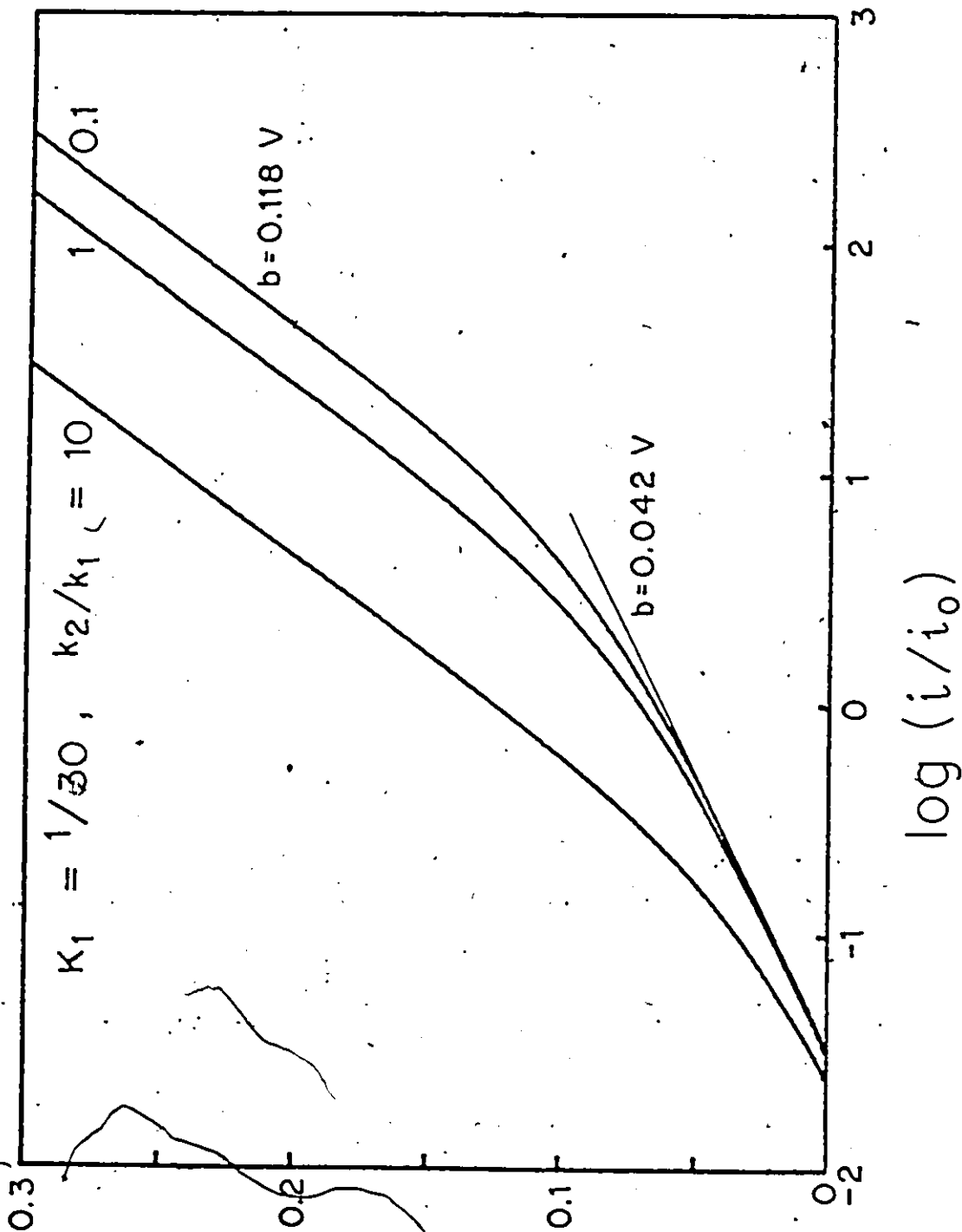


Fig. 4.15 Numerical simulation of Tafel plots for h.e.r. according to mechanism 4.1, 4.2 using the relation $i/i_0 = \theta_H \exp[\eta F / 2RT]$ with same values of parameters as for plots in Fig. 4.12.

From the data of Fig. 4.11, derived from the experimental decay behaviour, the self-consistency of the results can be demonstrated by back-calculating the corresponding expected Tafel relations, taking account of the variation of θ_H with η and using $\exp \eta F/2RT$ as the charge-transfer factor. The results of such calculations are shown in Fig. 4.16 from which it is seen that the 2-slope forms of the experimental Tafel plots (Figs. 4.1 a,b) are well reproduced and thus can be clearly experimentally attributed to the determined dependence of θ_H on η .

The mechanism of the h.e.r. at Ni in alkaline solution and the extent of H coverage during steady evolution of H_2 have hitherto been controversial questions^{64,166,188-190}. The present results now give a clear conclusion regarding this matter: at potentials more negative than $0.15 \sim 0.25$ V E_H , H_2 evolution at Ni wire or Ni-Mo-Cd electrodes from alkaline solutions proceeds on a surface that is appreciably covered, but to a limitingly constant < 1 , by the electroactive intermediate, adsorbed H, giving a Tafel slope 0.125 V while nearer the reversible potential, as coverage by H decreases, a potential-dependent pseudocapacitance is developed with a characteristic^{38,39,163} maximum giving a Tafel slope of $0.04 \sim 0.06$ at the Ni-Mo-Cd composite electrode. At Ni wire, the limiting θ_H is smaller than at Ni-Mo-Cd, and its potential dependence is evidently insufficient to give rise to a well defined lower slope region at this metal; however, near the reversible potential, after the back reaction current which complicates linearity of the Tafel relation, is subtracted out (Figs. 4.1 a,b),

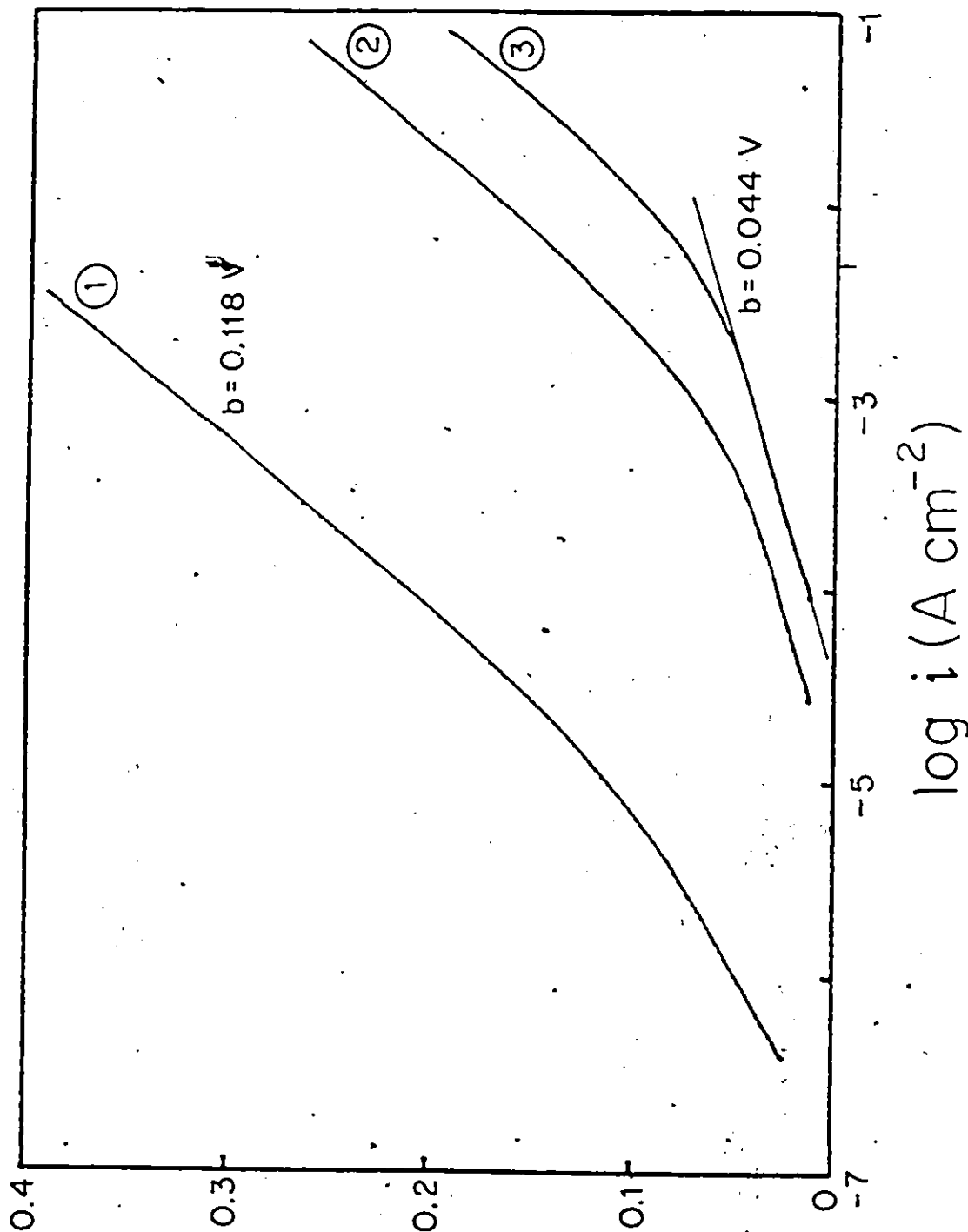


Fig. 4.16 Tafel relations derived from the experimentally determined θ_H as $f(n)$ from Fig. 4.11:
 1) Ni, 298 K, $i_0 = 1 \times 10^{-5}$ A cm⁻²; 2) Ni - Mo - Cd plated, 298 K, $i_0 = 1 \times 10^{-3}$ A apparent cm⁻²; 3) as in (3) but for 353 K.

the Tafel plot for the h.e.r. at Ni wire (Fig. 4.1a) does show some change of slope at low η values.

We see that the new method of analysis of potential decay leads, for the first time, to a rather complete experimental knowledge of the coverage and pseudocapacitance behaviour of the electroactive H intermediate in the h.e.r. proceeding at appreciable currents at Ni, a Ni-Mo bulk alloy and electrocoated Ni-Mo-Cd cathodes, as well as the condition of the kinetics of the steps in the overall reaction pathway in terms of the ratios of the rate constants involved.

4.1.1.6 Comparison of Polarization Behaviour of Ni-Mo-Cd and Ni Electrodes

The principal difference in polarization behaviour is the existence of a low-slope region at Ni-Mo-Cd that is not observed at Ni wire electrodes (Fig. 4.1) but the high current-density behaviour is evidently similar, allowing for the ratio of the electrochemical real/apparent area factors of ca. 220 X. This also corresponds to the capacitance behaviour (Figs. 4.7-9) where the double-layer capacitance is found to be about 250 X larger at the coated electrodes than at Ni. However, an additional difference that may be connected with the appearance of the low slope Tafel region at Ni-Mo-Cd is the trend to a relatively high capacitance between $\eta = -0.10$ and 0 V (Fig. 4.8) corresponding to the second linear region of the log C relation in Fig. 4.9. It is possible that within 0.1 V of the H_2 reversible potential,

the h.e.r. at Ni-Mo electrodeposits or Raney's proceeds through mediation of a decomposing hydride, as Conway and coworkers suggested¹⁴⁷ and as is supported by cyclic-voltammetry results at these materials. (See more detailed discussion in section 4.1.2.2 on the a.c. impedance work).

Evidently, the coated electrode does not differ just in real area; its method of preparation and composition, which may introduce a hydride phase through codeposition of H^{147,167,168}, has a major effect on the type of polarization behaviour observed and on the potential-dependence of the adsorption of H (compare slopes of the lines in Figures 2, 4 and 10). In the case of Ni-Mo, it should also be noted¹⁴⁷ that a bulk, thermally prepared alloy does not behave in the same way as an electrocoated material of the same nominal composition (see Fig. 4.1).

These observations clearly have important consequences for the possibility of preparing by electrocoating and other techniques various high-area electrode materials that differ electrocatalytically from the corresponding bulk substances other than because of the large real area.

4.1.1.7 Activation Energies

The apparent activation energies¹⁶⁵ for the two Tafel regions exhibited by the h.e.r. at Ni-Mo-Cd electrodes (Fig. 4.1) were obtained from the derivative $d \ln i_0 / d(1/T)$ of electrochemical Arrhenius plots, (see Fig. 4.17). As follows from Figure 4.17a, the activation energy for the low-slope region (17 kJ mol^{-1}) is

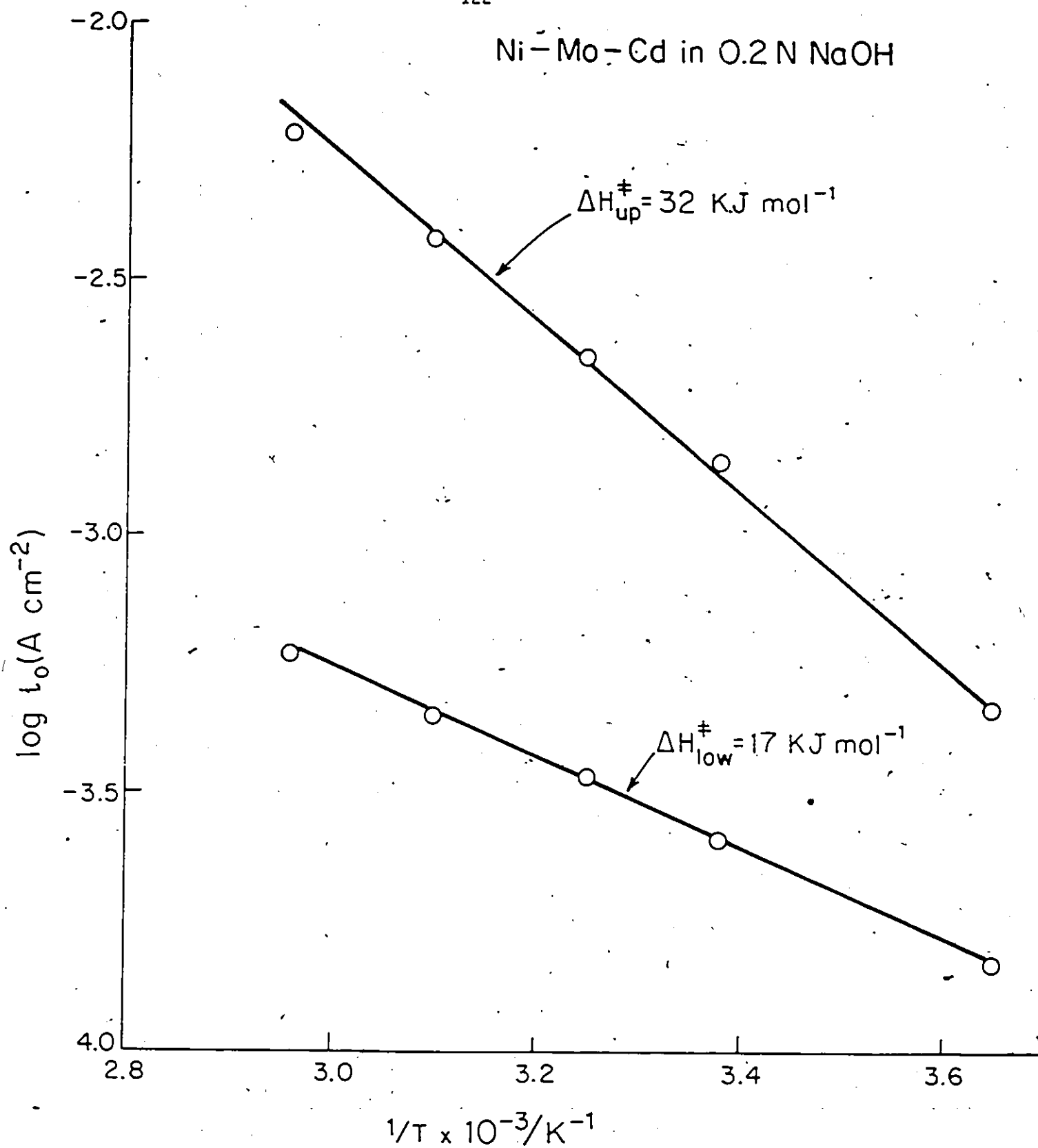


Fig. 4.17 a) Plots of $\log i_0$ vs $1/T$, electrochemical Arrhenius plots, for Ni-Mo-Cd electrode for the two Tafel regions.

Ni wire in 0.2 N NaOH

$$\Delta H^\ddagger = 35 \text{ KJ mol}^{-1}$$

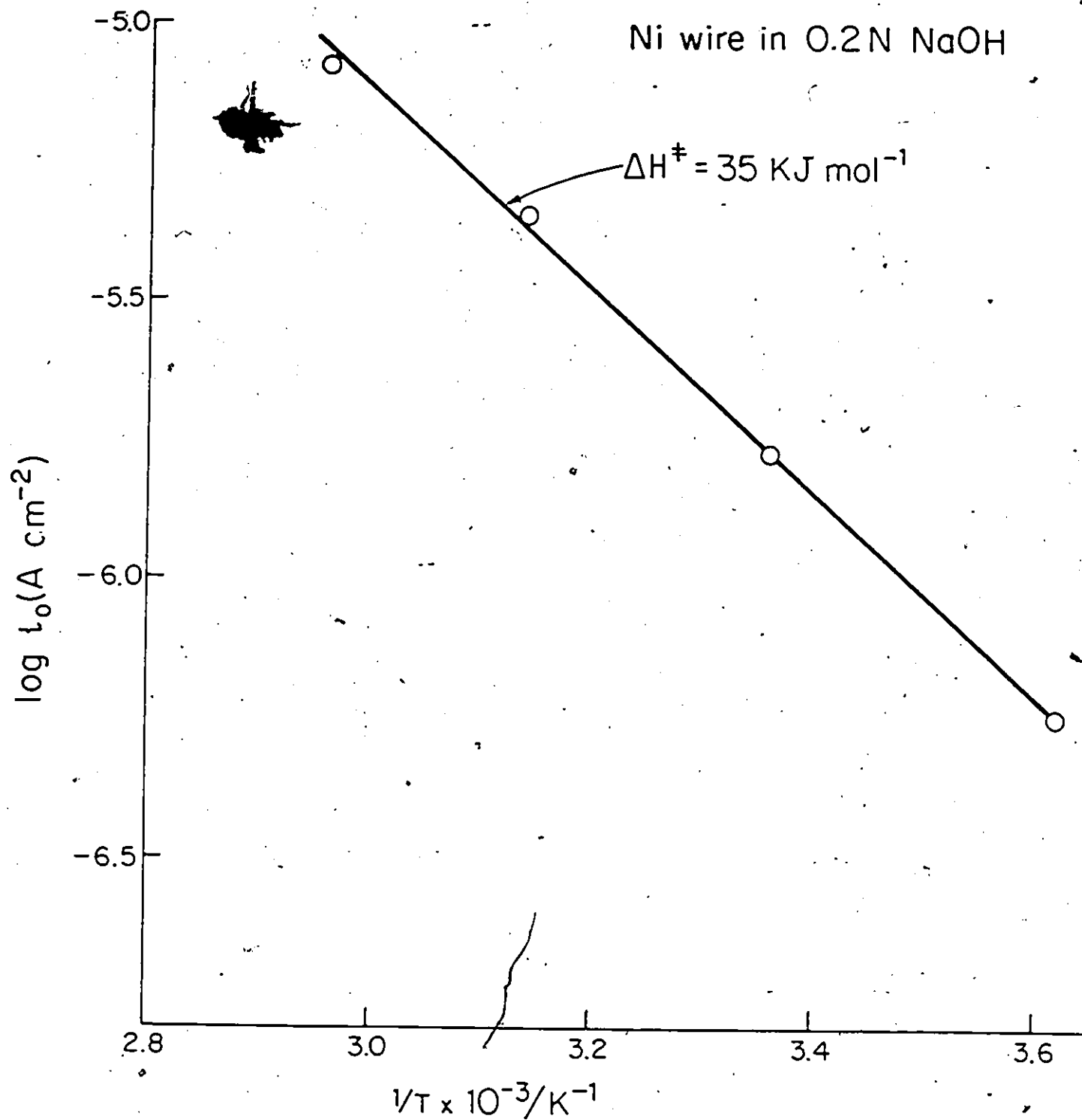


Fig. 4.17 b) Plots of $\log i_0$ vs $1/T$ for pure Ni electrode.

much lower than that for the higher-slope sections (32 kJ mol^{-1}). This is the basis of the practically important situation that low Tafel slopes increasingly characterize the polarization behaviour of Ni-Mo-Cd electrode preparations as the temperature is raised (Fig. 4.1). The $\Delta H^\ddagger (\eta = 0)$ for the h.e.r. at Ni wire electrodes is ca. 35 kJ mol^{-1} , (see Fig. 4.17b), and the same value characterizes the Tafel relation from 10^{-6} to $2 \times 10^{-2} \text{ A cm}^{-2}$. The activation energy at $\eta = 0$ for Ni-Mo-Cd cathodes (32 kJ mol^{-1}) is quite similar to that at Ni wire (35 kJ mol^{-1}) derived from the Tafel relations at high η , which suggests that over this region the reaction conditions are the same at these two materials, i.e. the h.e.r. proceeds on a surface whose coverage by H is incomplete but limitingly constant with further increase of η . At low η , for Ni-Mo-Cd electrocoated electrodes, the activation energy (17 kJ mol^{-1}) is lower which corresponds to the h.e.r. proceeding on a surface where θ_H is potential-dependent and has not yet attained its constant limiting value. Under these conditions θ_H , at a given η , as well as the rate constant k_2 , can be temperature-dependent, leading to a different value of $\Delta H^\ddagger$ from that at high η . Alternatively, the $\Delta H^\ddagger$ for the low η region may correspond (cf. ref. 147) to a different mechanism of H desorption involving a surface hydride, (see below section 4.1.2.2).

4.1.2 Results from the a.c. impedance method

The basis for treatment of the results for the h.e.r. using a.c. impedance measurements was as described in section 3.2, using the development of Armstrong's approach^{129,130} described in that chapter.

4.1.2.1 Ni in 0.5M NaOH

In Fig. 4.18, curve 1 is the steady-state polarization Tafel plot, and curve 2 the $\log (1/R_{\infty})$ vs η impedance plot*. The points represent the experimentally measured data obtained in 0.5M NaOH solution at Ni wire electrode (real surface area 0.66 cm^2 , taking the roughness factor equal to 2, see section 4.1.1) at 296K. The solid line 1 is the simulated Tafel plot using eqn. (3.41) and the solid lines 2 and 3 are the simulated impedance plots of $\log (1/R_{\infty})$ and $\log (1/R_p)$ vs η , respectively, using eq. (3.42) with the following rate constant values: $k_1 = 1.5 \times 10^{-11}$; $k_{-1} = 7 \times 10^{-11}$; $k_2 = 1.5 \times 10^{-11}$; $k_3 = 1.5 \times 10^{-13} \text{ mol cm}^{-2} \text{ s}^{-1}$. The good agreement between experimental and simulated results in Fig. 4.18 suggests that the reaction model proposed here describes the real systems quite well (and for the following results too). The ratio of $k_2/k_3 = 100$, required to represent the observed behaviour, implies that the contribution of the recombination step (eqn. 1.8) to the total steady-state current is negligible for the h.e.r. at Ni electrode.

Fig. 4.18 shows that both experimentally and by simulation, the η vs $\log i$ and η vs $\log (1/R_{\infty})$ plots (on the log scale - curves 1 and 2 of Fig. 4.18) become two parallel lines with a slope of 0.12 V that are separated by a value of 1.24. This behaviour can be rationalized by our own reaction models, as follows: from eqn. (3.41), for sufficiently high η and constant θ_H , the rate of the recombination step and thus its contribution to the overall desorption rate becomes negligible; then

* See p. 75 for definition of R_{∞} and R_p .

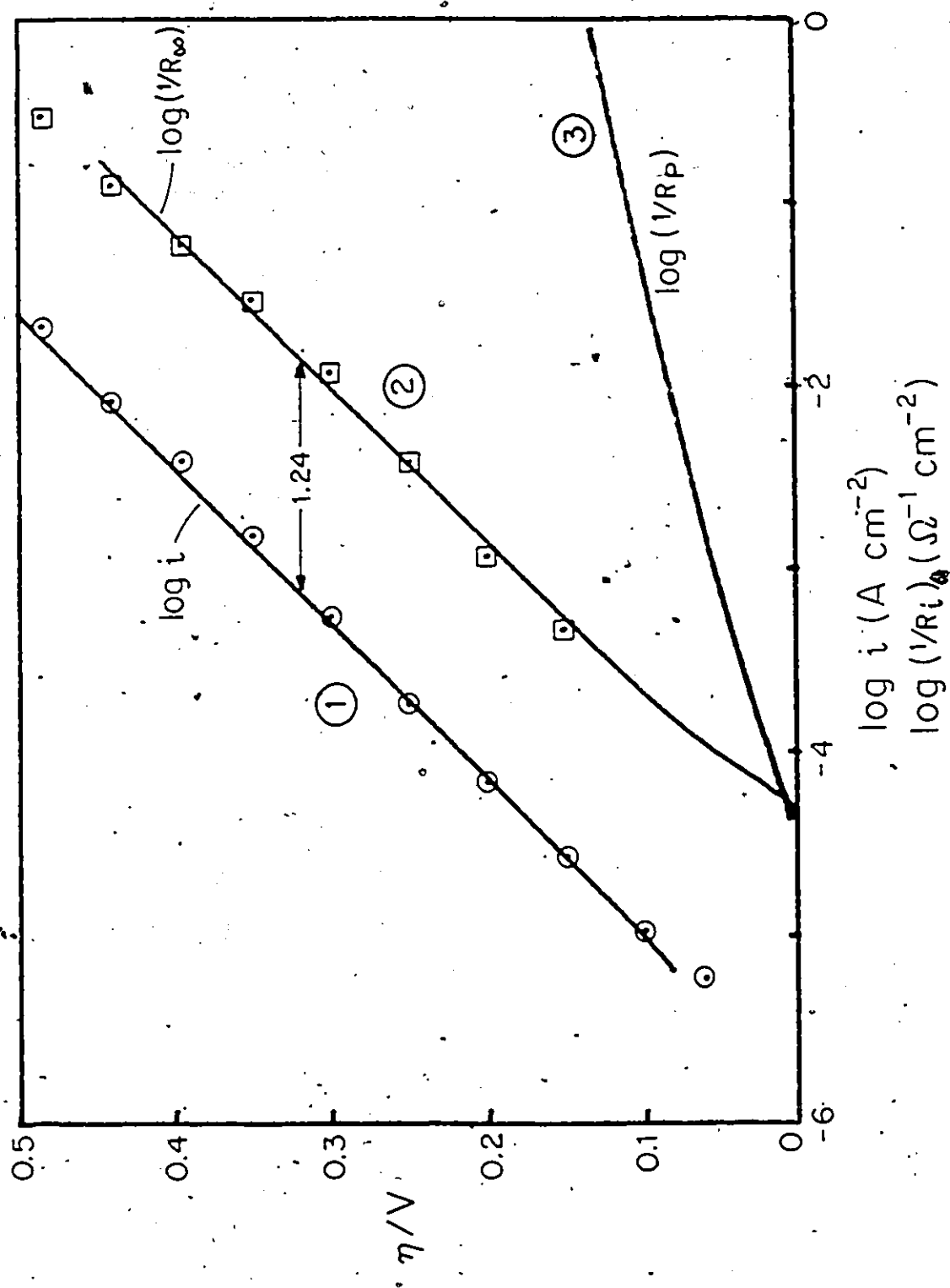


Fig. 4.18 Experimental and simulated Tafel plots (1) and $\log (1/R_i)$ vs r plots (2,3) for the h.e.r. at Ni wire electrode in 0.5 M NaOH aq. solution. The points represent the experimentally measured data and solid lines are the simulated plots. $R_i = R_\infty$ in curve 2; $R_i = R_p$ in curve 3.

$$\left(\frac{di}{d\eta}\right)_{\theta_H} = \text{constant} = (BF/RT) i \quad (4.14)$$

From eqn. (3.26b) (also see eqn. (3.36)), at sufficiently low frequency:

$$\left(\frac{di}{d\eta}\right)_{\omega=0} = (Y_f)_{\omega=0} = 1/R_p + 1/R_\infty = 1/(R_p + R_\infty) \quad (4.15)$$

Thus, at high η and $\omega = 0$:

$$\log[1/(R_\infty + R_p)] = \log i + \log(BF/RT) \quad (4.16)$$

with $\beta = 0.5$ and $T = 300\text{K}$, $\log(BF/RT) = 1.28$, which is close to the experimentally observed value of 1.24.

Since R_p becomes extremely small when $\eta > 0.1\text{ V}$ for the h.e.r. at Ni (See Fig. 4.18), $1/(R_\infty + R_p) \approx 1/R_\infty$. This result is not, however, surprising; because $R_\infty + R_p$ is the total Faradaic resistance, its reciprocal should be directly related to the Faradaic current at that potential. The slopes equal to 0.12 V suggest that the overall reaction is kinetically controlled by the electrochemical desorption step, although control by the discharge step would also give $b = 0.12\text{ V}$; however, it would be associated with very small H coverage which is not true for this present case (see below, Fig. 4.21). The simulated behaviour with $k_1 = k_2$ in this case agrees with the conclusion from the potential-decay results (see 4.1.1.4).

Fig. 4.19 shows the complex-plane impedance diagrams for $\eta =$ a) 0.045; b) 0.20; c) 0.30 and d) 0.395 V. The experimental data are represented by circled points for which the underlined numbers give, in the usual way, the respective frequencies. The conditions are the same as for Fig. 4.18. The points connected by solid

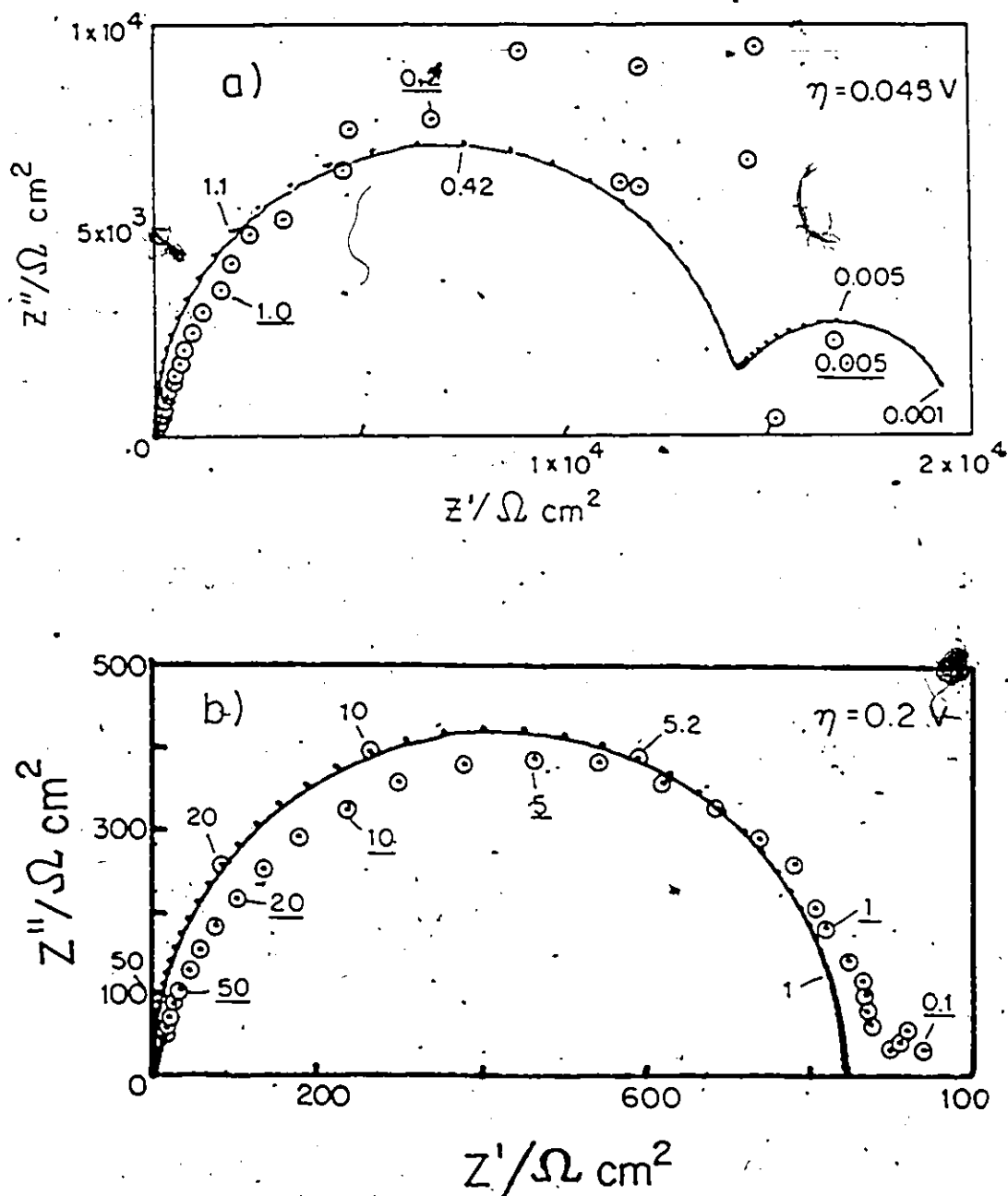


Fig. 4.19 Experimental (circled points) and simulated (solid lines) a.c. impedance spectra plotted in the complex-plane, for the same conditions as in Fig. 4.18, the numbers representing the respective frequencies (underlined for experimental data), for four d.c. overpotentials: (a) $\eta = 0.045 \text{ V}$, (b) $\eta = 0.20 \text{ V}$ (c, d see next page).

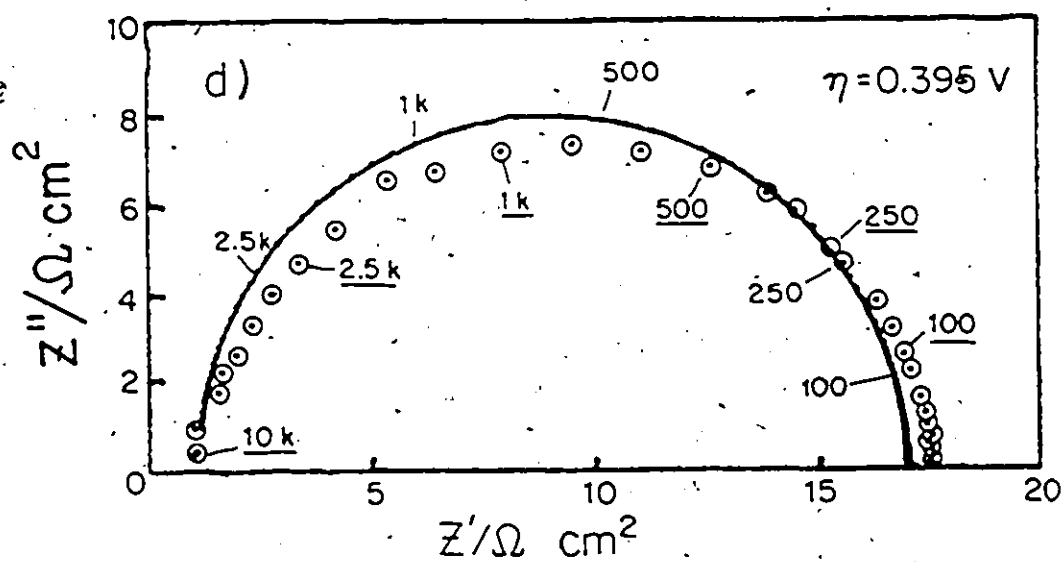
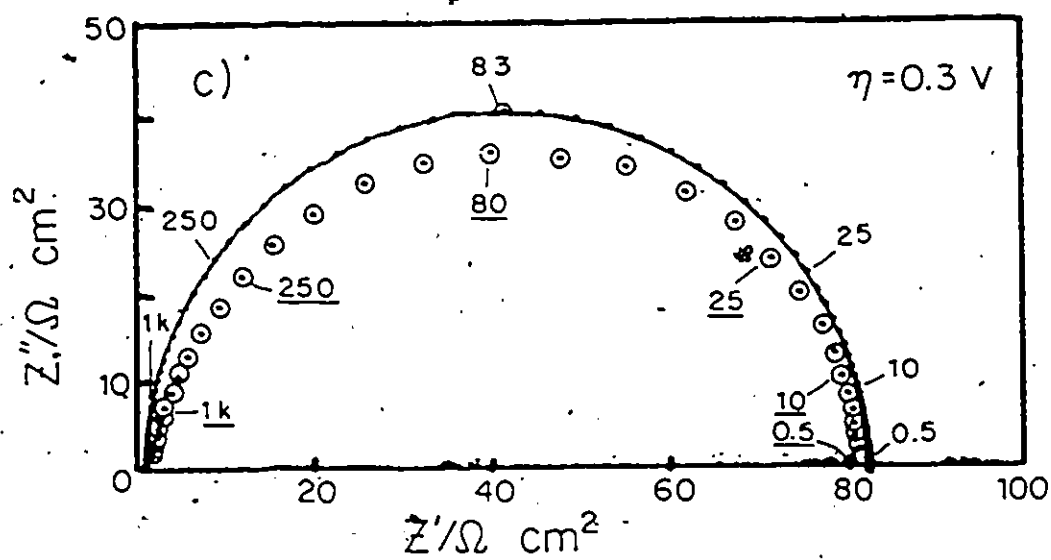


Fig. 4.19 (continued) (c) $\eta = 0.30 \text{ V}$, (d) $\eta = 0.395 \text{ V}$.

lines without circles represent the behaviour simulated by eqns. (3.29) and (3.42) with the same set of rate constants as for Fig. 4.18, taking $C_{dl} = 25 \mu F cm^{-2}$, $q_1 = 250 \mu C cm^{-2}$ and $R_s = 1.1 \Omega$.

The impedance spectra for the h.e.r. at Ni in Fig. 4.19 are single semi-circles for most of the d.c. polarization potentials, except a) at the low potential $\eta = 0.045 V$, where the behaviour is similar to that in previous studies for the h.e.r. at Fe^{160} and W , WC^{131} . The single semi-circle impedance spectra in the complex-plane suggests that only C_{dl} and R_∞ in parallel are the significant components in the equivalent circuit (see Fig. 3.4) and no adsorption pseudo-capacitance C_ϕ is involved. This may be the true condition for the h.e.r. at Ni at high overpotentials and is consistent with the Tafel plot (curve 1 in Fig. 1.8), which implies that θ_H almost reaches a constant value as $\eta > 0.15 V$, and with the results of the potential-decay experiments (see 4.1.1.3 and Fig. 4.7).

From the results of the potential decay measurements, C_ϕ is significant at low overpotentials, $0 < \eta < 0.15 V$, for the h.e.r. at Ni (see Fig. 4.7). This implies that a second semi-circle should appear in the impedance diagram due to the relaxation associated with the H adsorption process. This can be seen from the simulated plot (solid line in Fig. 19a) for $\eta = 0.045 V$. However, experimentally, on account of the high Faradaic resistance ($R_f = 2 \times 10^4 \Omega cm^2$) at this potential, the frequency must go down to $0.001 Hz$ for the effect of this C_ϕ to be detected. Unfortunately, at such low frequency, the experimental resolution is inadequate for the second adsorption semi-circle to be distinguished in relation to the inherent noise (points with circles in Fig. 4.19a)*.

* Note that the scattering of data is much smaller at the high η values (see Figs. 4.19 b, c and d); this is due to the much smaller Faradaic resistances and the corresponding higher resolution of the instrument for the resulting smaller "RC" time-constants of the electrode processes.

Fig. 4.20 shows the Bode plots (without corresponding phase plots). The experimental conditions and theoretical parameters for curves 1, 2, 3 and 4 in Fig. 4.20 are the same as those for curves a, b, c and d in Fig. 4.19, respectively. It is seen that the numerically simulated behaviour (solid line in Fig. 4.20), provides a very good fit to the experimental data (points in Fig. 4.20), except for curve 1 at the low frequency end, which corresponds to the "noise" data in diagram (a) of Fig. 4.19.

The pseudocapacitance, C_ϕ , can however, be calculated from the rate constants using eqn. (3.40). Fig. 4.21 shows simulated C_ϕ , C_p , τ vs η plots, using eqn. (3.40-3.43), with the same values of the rate constants and other parameters as in Figs. 4.18 and 4.19. The C_ϕ vs η plot has a peak at ca. 0.05V then exponentially decreases and reaches zero at ca. 0.2V, which is quite similar to the experimentally determined behavior derived with the potential decay method under the same conditions (see Fig. 4.7). The C_p vs η plot, which has a similar shape to that of the C_ϕ vs η plot only at very low values (this cannot be seen in Fig. 4.21), exponentially increases, reaching a value of $6 \times 10^6 \text{ F cm}^{-2}$ at $\eta = 0.3 \text{ V}$. As was shown in section 3.2.2.2, C_p is not a true measure of the variation of adsorbed charge with potential under a.c. conditions, but its values may be quite close to C_ϕ under some conditions. On the other hand, the τ (see eqn. 3.42) vs η profile is very similar to the C_ϕ vs η plot; this is reasonable since τ is a relaxation time constant for passage of the deposition/desorption charge for H and thus measures how rapidly θ_H relaxes to its new value after the potential is

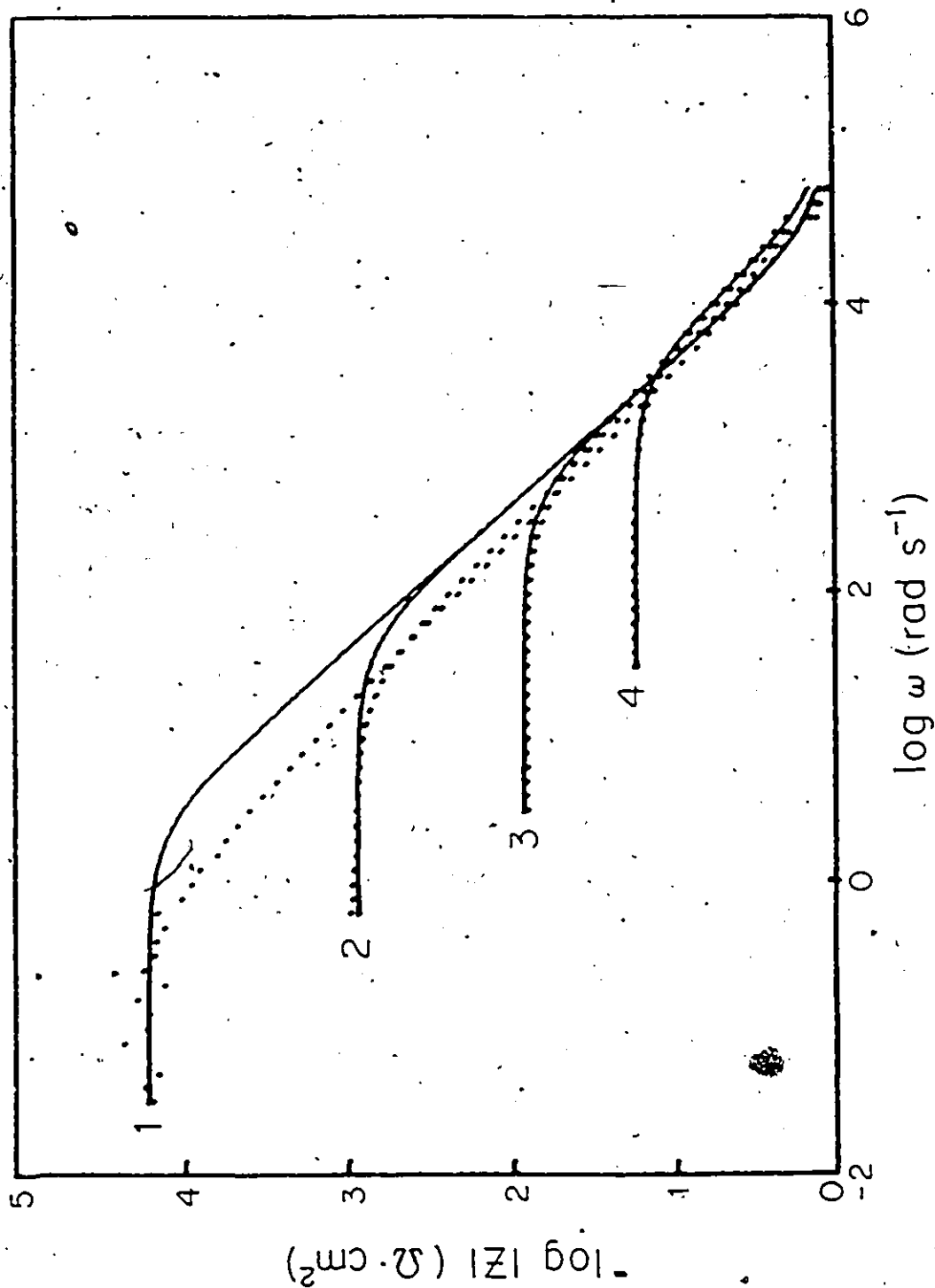


Fig. 4.20 Experimental (points) and simulated (solid lines) Bode plots (without corresponding phase plots) for the h.e.r. at Ni wire electrode in 0.5 M NaOH aq. solution. The experimental conditions and theoretical parameters for curves 1, 2, 3 and 4 are the same as those for curves a, b, c and d in Fig. 4.19, respectively.

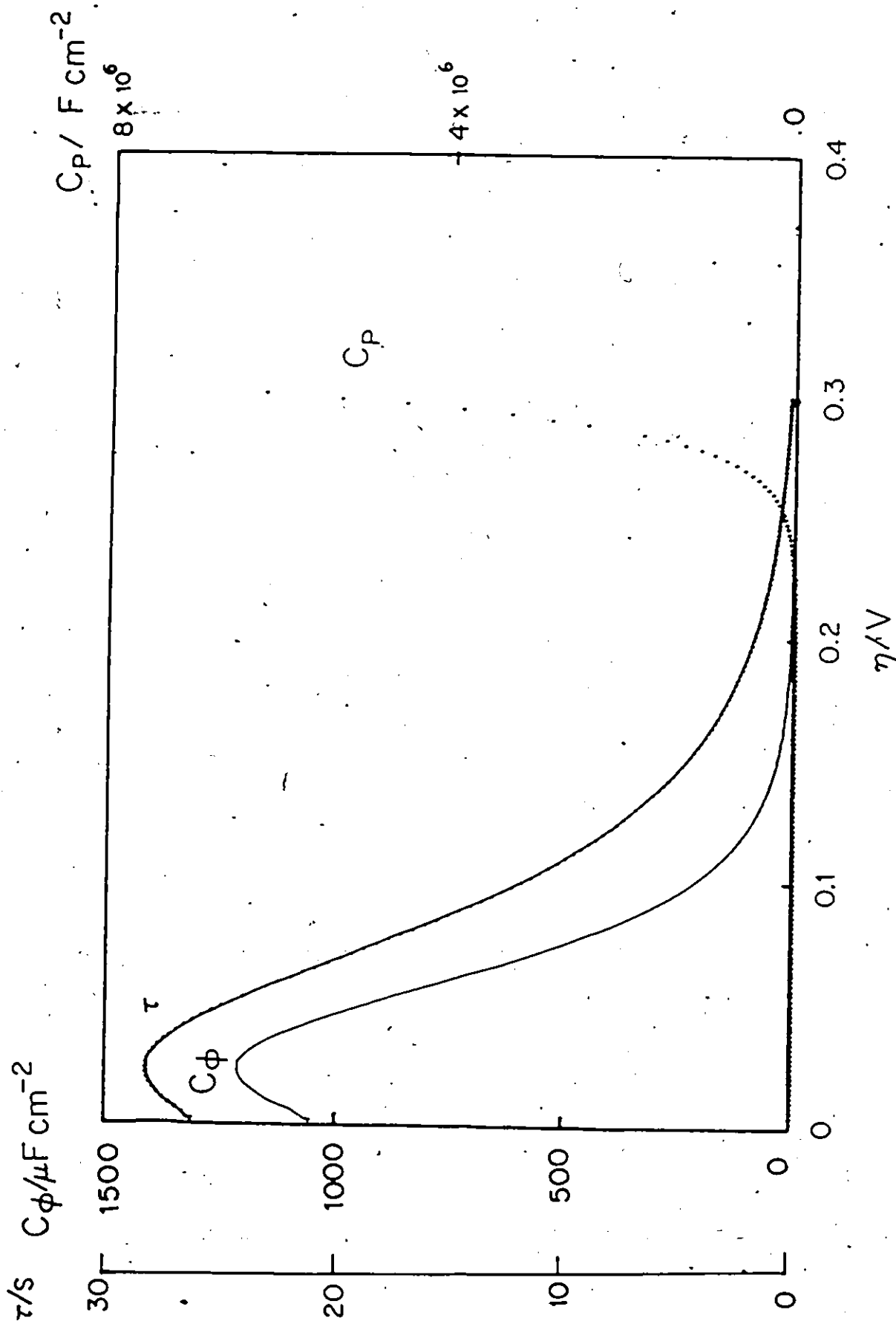


Fig. 4.21 Simulated C_ϕ , C_p , τ vs η plots, using eqns. (3.40-3.43), with same values of the rate constants and other parameters as in Figs 4.18 and 4.19.

changed, i.e. τ has a physical significance similar to that of C_ϕ .

4.1.2.2 Ni-Mo-Cd in 0.5 M NaOH

From earlier exploratory work on the electrochemical behaviors of electroplated Ni-Mo-Cd alloys¹⁴⁷, it was suggested that the observed potential decay results at low overpotential might be explained in terms of the role of an electrolytically formed hydride phase. The present work provides some further strong and more quantitative evidence in support of the existence of such an hydride.

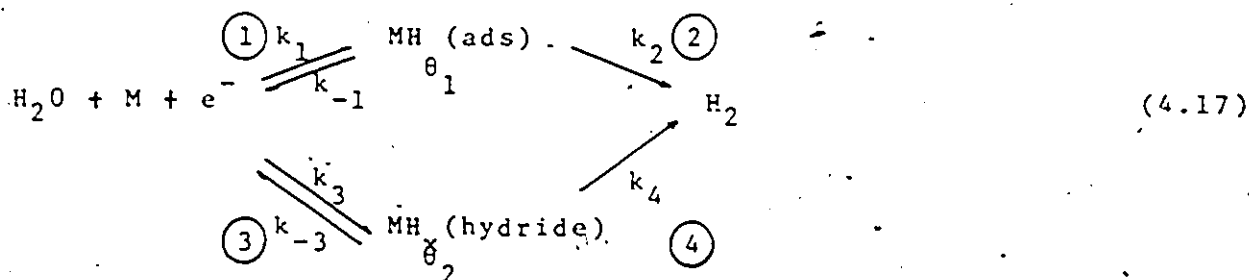
One aspect of the evidence is clearly shown by the potential decay results expressed in terms of the derived $\log C(\eta)$ vs η plots (see Fig. 4.9). In Fig. 4.9, the η -dependent behavior corresponds to that of three potential-dependent capacitances giving distinguishable time-domains of the η vs $\log t$ plot. The first corresponds to the influences of the double-layer capacitance which is potential independent and thus has a flat $\log C$ vs η plot (see curve in Fig. 4.9 for pure Ni wire at 276K in the potential range 0.25-0.40V). The second is the pseudocapitance, C_ϕ , which is important over the potential range 0-0.25V, and has almost the same potential dependence for the three electrodes of different materials (same slopes in Fig. 4.9). The third is the capacitance, C_{hyd} , that we suggest is due to a sorption process associated with hydride formation and decomposition which can be seen clearly for the Ni-Mo-Cd plated electrode at 278K in Fig. 4.9 with a much steeper $d\log C/d\eta$ slope over the potential range

0-0.1V, giving rise to large C values.

Further evidence for the participation of an hydride process is afforded by the appearance of the third semi-circle in the impedance complex-plane spectra (see Fig. 4.23) which could be due to an hydride pseudocapacitance, C_{hyd} . (The C_{hyd} would formally originate from a potential-dependence of the extent of H sorbed into the surface region of the electrode on potential, near the H_2 reversible potential and would probably be a slow process, resolvable only at low frequency).

The hydride phase may originate in preparation of the Ni-Mo-Cd material by co-deposition of the nickel and molybdenum which takes place with inevitable simultaneous discharge of hydrogen. This probably is the key to the observed favorable electrocatalytic activity of these materials (possibly for Pt too, see section 4.3) associated with the low-slope behavior of the log (current) vs voltage relation, giving good polarization performance at elevated current-densities.

For this situation, a reaction model can be proposed as follows:



where θ_1 and θ_2 are the fractional occupancies of the 2- and 3-dimensional lattices available for H sorption (the surface and

the hydride phase, respectively). The kinetic involvement of an hydride phase may be through itself as a reaction intermediate¹⁴⁷ or through a change the electrocatalytic properties of the 2d-surface on which the o.p.d. of H arises, giving rise to a surface which is adsorptively different from metal sites available for H chemisorption on the regular metal surface.

The rate equations for each step in diagram (4.17) can be written as:

$$v_1 = k_1(1-\theta_1)\exp(\beta F\eta/RT) - k_{-1}\theta_1\exp(-(1-\beta)F\eta/RT) \quad (4.18a)$$

$$v_2 = k_2\theta_1\exp(\beta F\eta/RT) \quad (4.18b)$$

$$v_3 = k_3(1-\theta_2)\exp(\beta F\eta/RT) - k_{-3}\theta_2\exp(-(1-\beta)F\eta/RT) \quad (4.18c)$$

$$v_4 = k_4\theta_2^2 \quad (4.18d)$$

The steady-state current is given by

$$i = 2F(k_2\theta_1\exp(\beta F\eta/RT) + k_4\theta_2^2) \quad (4.19)$$

Step 2 in diagram (4.17) is a electrochemical-desorption step, since the observed Tafel slope is 0.125V at high η ; step 4 is the recombination desorption step, since a) the Tafel plots have a low slope (40-50mV) at low η ; b) the contribution from this step reaches a limit when η becomes high ($\theta \rightarrow 1$ or constant).

Following the steady-state approach similar to the treatment given earlier, θ_1 and $C_{\phi,1}$ are of the same form as given by eqns. (4.8) and (4.9), respectively; θ_2 and $C_{\phi,2}$ are of the same form as eqns. (3.39) and (3.40), respectively, except that there no λ_2 term is involved.

The Faradaic admittance is given by:

$$\tilde{Y}_f = 1/R_\infty + 1/\{R_{o,1}(1+\omega^2\tau_1^2)\} + 1/\{R_{o,2}(1+\omega^2\tau_2^2)\} - j[\omega\tau_1/\{R_{o,1}(1+\omega^2\tau_1^2)\} + \omega\tau_2/\{R_{o,2}(1+\omega^2\tau_2^2)\}] \quad (4.20)$$

where

$$1/R_{\infty} = F\{(\partial v_1/\partial E)_{\theta_1} + (\partial v_2/\partial E)_{\theta_2} + (\partial v_3/\partial E)_{\theta_2}\}$$

$$1/R_{o,1} = (F^2\tau_1/q_1)\{(\partial v_1/\partial \theta_1)_E + (\partial v_2/\partial \theta_1)_E\}\{(\partial v_1/\partial E)_{\theta_1} - (\partial v_2/\partial E)_{\theta_1}\}$$

$$1/R_{o,2} = (F^2\tau_2/q_2) (\partial v_3/\partial \theta_2)_E (\partial v_3/\partial E)_{\theta_2}$$

$$1/\tau_1 = (F/q_1)\{(\partial v_2/\partial \theta_1)_E - (\partial v_1/\partial \theta_1)_E\}$$

$$1/\tau_2 = (F/q_1)\{(\partial v_4/\partial \theta_2)_E - (\partial v_3/\partial \theta_2)_E\}$$

q_1 and q_2 are the charges required for full occupancy, $\theta_1 = 1$, and $\theta_2 = 1$ of the 2d and 3d lattices, respectively. Notice there are two relaxation times and two R_o values are involved, which together with C_{dl} , give the possibility for three semi-circles to appear in the complex-plane representation of the impedance behavior of the h.e.r. at the Ni-Mo-Cd electrodes, as is actually observed under certain conditions (low η).

The results calculated from eqns. (4.20) and (4.18), as two examples of complex-plane plots, are shown in Fig. 4.22. The rate constants and other parameters are arbitrarily taken: (a) $k_1 = 10^{-7}$; $k_{-1} = 10^{-6}$; $k_2 = 10^{-9}$; $k_3 = 10^{-7}$; and $k_{-3} = 10^{-6}$ and $k_4 = 10^{-6} \text{ mol cm}^{-2} \text{ s}^{-1}$, $q_1 = 2.5$; $q_2 = 250 \text{ mc cm}^{-2}$ and $C_{dl} = 2.5 \text{ mF cm}^{-2}$, (b) $k_1 = 10^{-9}$; $k_{-1} = 10^{-8}$; $k_2 = 10^{-11}$; $k_3 = 10^{-10}$; $k_{-3} = 10^{-9}$ and $k_4 = 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}$, $q_1 = 50 \text{ } \mu\text{C cm}^{-2}$; $q_2 = 50 \text{ mC cm}^{-2}$, $C_{dl} = 25 \text{ } \mu\text{F cm}^{-2}$. The value of η is 0.050V for both cases, (a) and (b). Fig. 4.22 shows clearly that three semi-circles arise which corresponds to two different adsorbed or sorbed intermediates and double-layer capacitance. The shapes of the

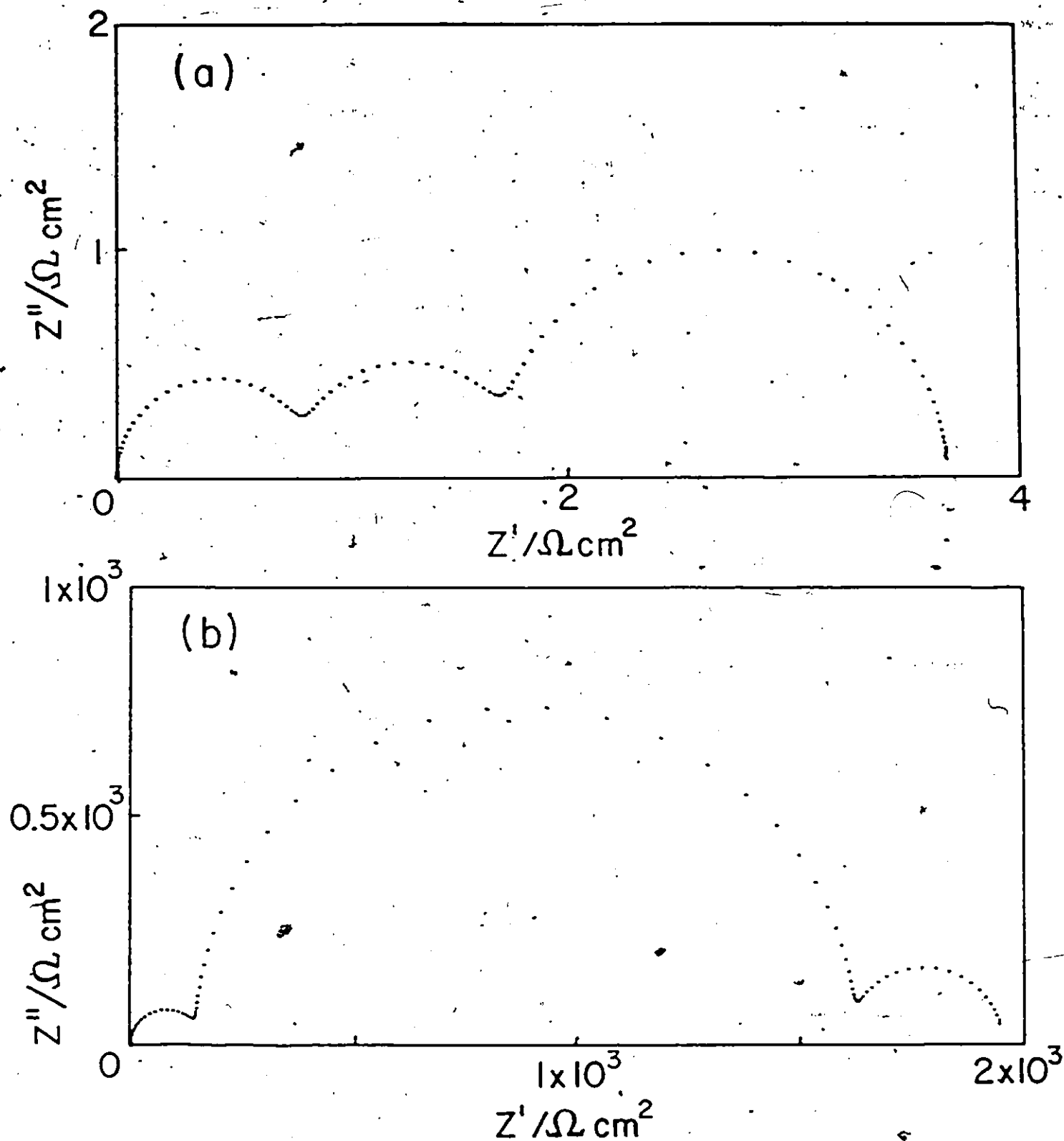


Fig. 4.22 Calculated impedance complex-plane plots by using model 4.17 with two relaxation time constants (two adsorbed reaction intermediates).

complex-plane plots or the frequency dispersion of the impedance depend on the values of the rate constants, relaxation times

τ_1 , τ_2 and C_{dl} .

It is interesting, now, to see whether the reaction model (4.17) and (4.18) can fit the experimentally observed data or not. Fig. 4.23 shows the complex-plane impedance diagrams for η - a) 0.058; b) 0.093; c) 0.145 and d) 0.230 V in the case of the h.e.r. at the Ni-Mo-Cd plated electrode in 0.5M NaOH at 296K. The experimental data are represented by the circled points and the numbers labeled in the diagrams (the underlined numbers for experimental data) are the corresponding frequencies (in Hz). The points without circles represent the behaviour simulated by eqn. (4.20) using the following rate constant values: $k_1 = 5 \times 10^{-7}$; $k_{-1} = 5 \times 10^{-6}$; $k_2 = 5 \times 10^{-9}$; $k_3 = 2 \times 10^{-8}$; $k_{-3} = 2 \times 10^{-7}$ and $k_4 = 2.5 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}$ and $C_{dl} = 2.5 \text{ mF cm}^{-2}$. The third semi-circle can be observed at low η (Fig. 4.23 a,b) when f goes down to 0.0025 Hz; this region gradually disappears or is obscured as η is increased (Fig. 4.23 c,d). At the high f end, the experimentally measured impedance spectra in Fig. 4.23 exhibit "distorted semi-circles" as observed by Armstrong and Bell¹³¹ for the h.e.r. at W, WC electrodes, and by Epelboin, Keddam and Lestrate¹⁸⁰ for iron dissolution reactions.

The three-capacitance component behavior also can be seen in Bode plots shown in Fig. 4.24. Fig. 4.24a is the phase vs $\log \omega$ while Fig. 4.24b is the $\log |Z|$ vs $\log \omega$ plots. The points are the experimental data, the same as in Fig. 4.23a, and solid lines are simulated curves obtained by using the same rate constants and other parameters as in Fig. 4.23a ($\eta = 0.058\text{V}$). The three peaks

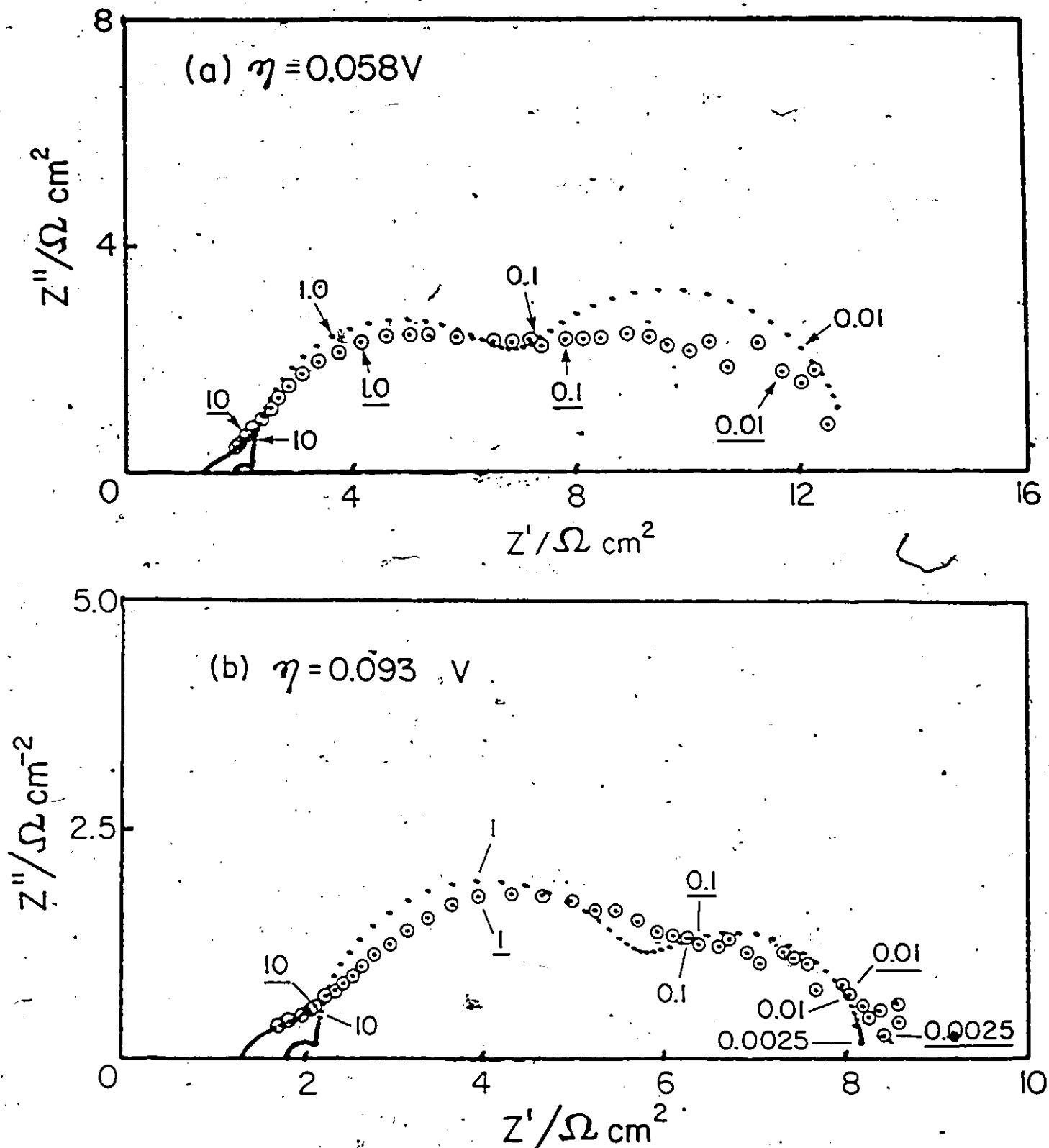


Fig. 4.23 Experimental (circled points) and simulated (points without circles) complex-plane impedance diagrams for the h.e.r. at Ni-Mo-Cd plated electrode, in 0.5 M NaOH at 296K, for four d.c. overpotentials: η = a) 0.058; b) 0.093 V; c) 0.145 and d) 0.230 V (c, d see next page).

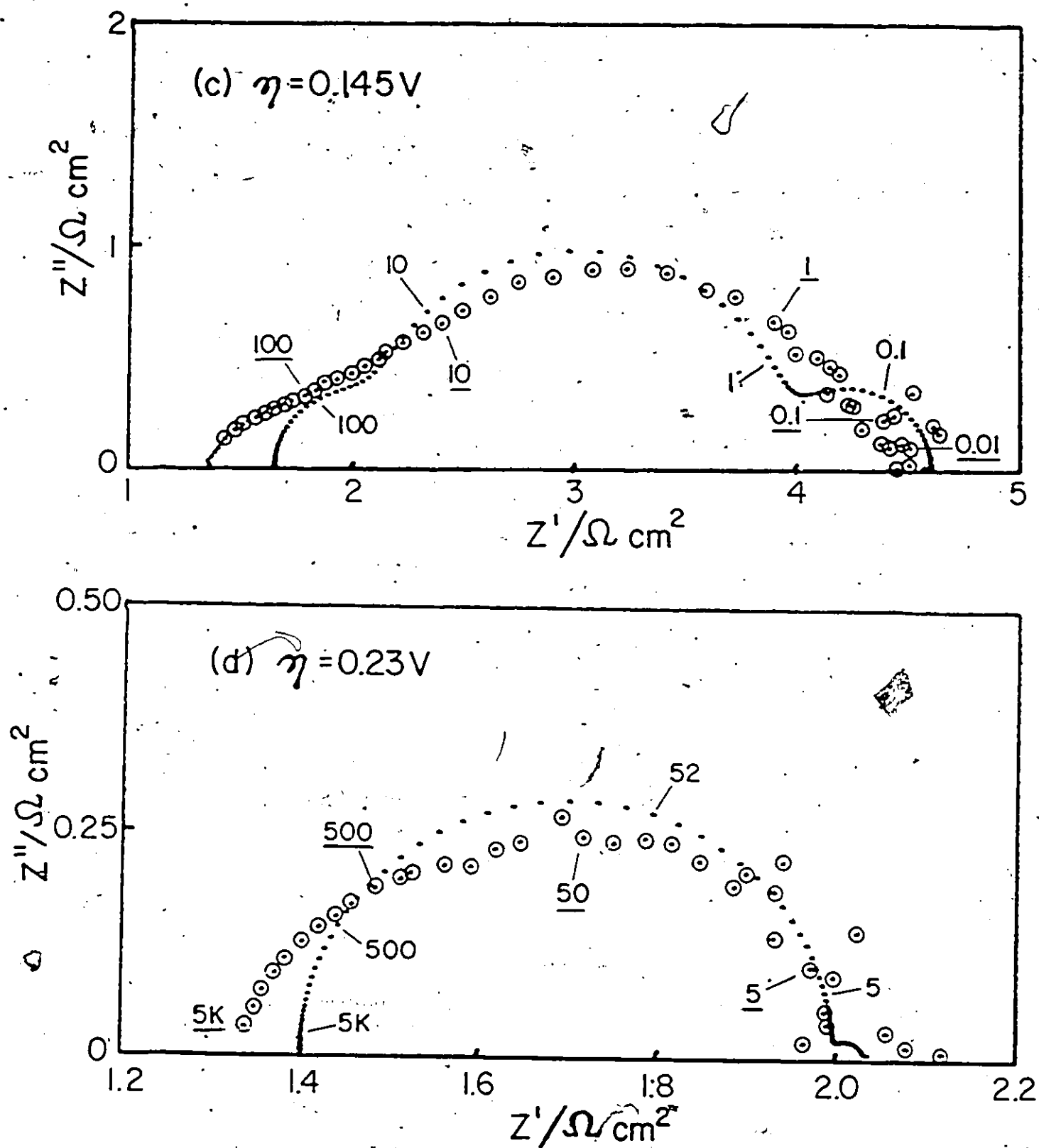


Fig. 4.23 (c, d) The numbers labeled in the diagrams (underlined numbers for experimental data) are the corresponding frequencies (in Hz).

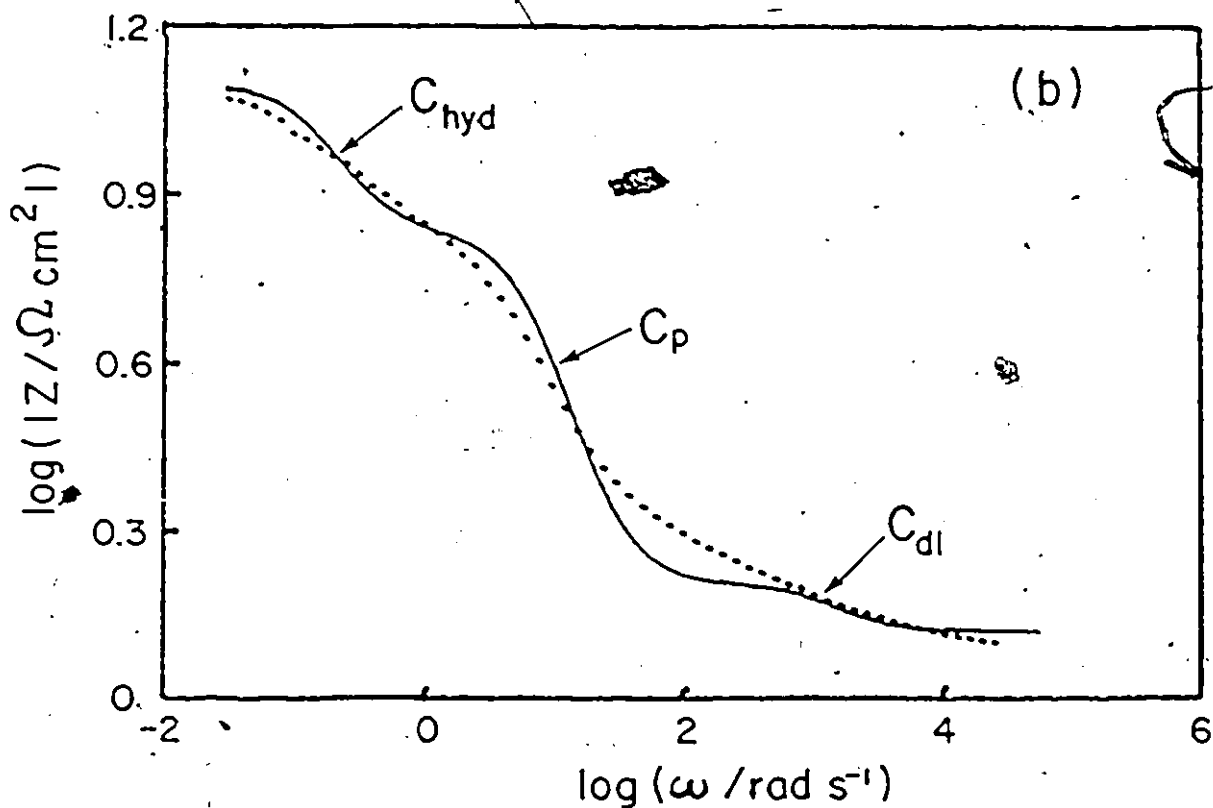
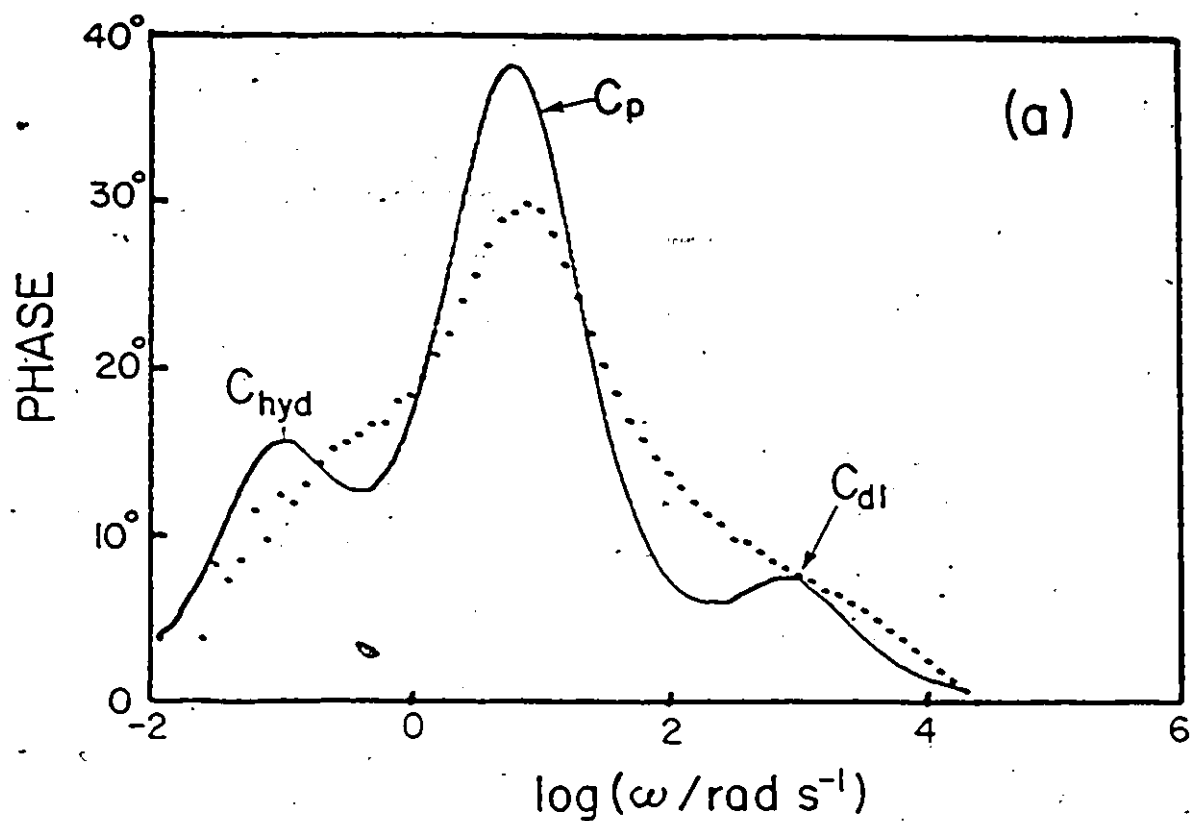


Fig. 4.24 Experimental (points) and simulated (solid lines) Bode plots for the same data and rate constants as in Fig. 4.23(a). Diagram a is the phase vs $\log \omega$ while b is the $\log |Z|$ vs $\log \omega$ plots.

in the phase plot (a) and three declining region in the $\log|Z|$ plot (b) are correspond to the influence of C_{dl} , C_p and C_{hyd} , respectively, as indicated in Fig. 4.24. Since the three capacitances have different magnitudes, their influences appear at different frequency regions in the Bode plots.

The simulated value of C_{dl} for the plated Ni-Mo-Cd electrode is 2.5 mF cm^{-2} which is 100 times larger than that for Ni ($25 \text{ } \mu\text{F cm}^{-2}$, see section 4.1.2.1). These data suggest that the "real" surface area of the plated Ni-Mo-Cd electrode is 100 times larger than that of the metallic Ni electrode. Comparing the ratio of real/apparent area = 450 from the BET method, we can conclude that about 25% of the "pores" in Ni-Mo-Cd electrode are "wetted", i.e. ca. 25% of the pores are the active sites for the electrochemical reaction. (The potential decay method gives ca. 50% wetted pores, see section 4.1.1.6).

In Fig. 4.25, the points with circles are the experimental Tafel data and the solid line 1 is the simulated Tafel plot by using eqn. (4.19) with the rate constants same as above. The solid curve 2 in Fig. 4.25 is the calculated current component which has a slope of 0.118 V at high η contributed by the "electrochemical desorption step" (taking the same rate constants as for curves 1 but $k_4 = 0$) while the solid curve 3 is the calculated current component which reaches a limit contributed by the "recombination step" (taking $k_2 = 0$). Fig. 4.25 shows that the sum of the data corresponding to curves 2 and 3 (curve 1) fits the experimental very well, especially the characteristic low slope at low η and the slope of 0.125 V at high η . The curve 3 is the contribution from the hydride (path 4 in diagram 4.17) at 296 K. We may expect that

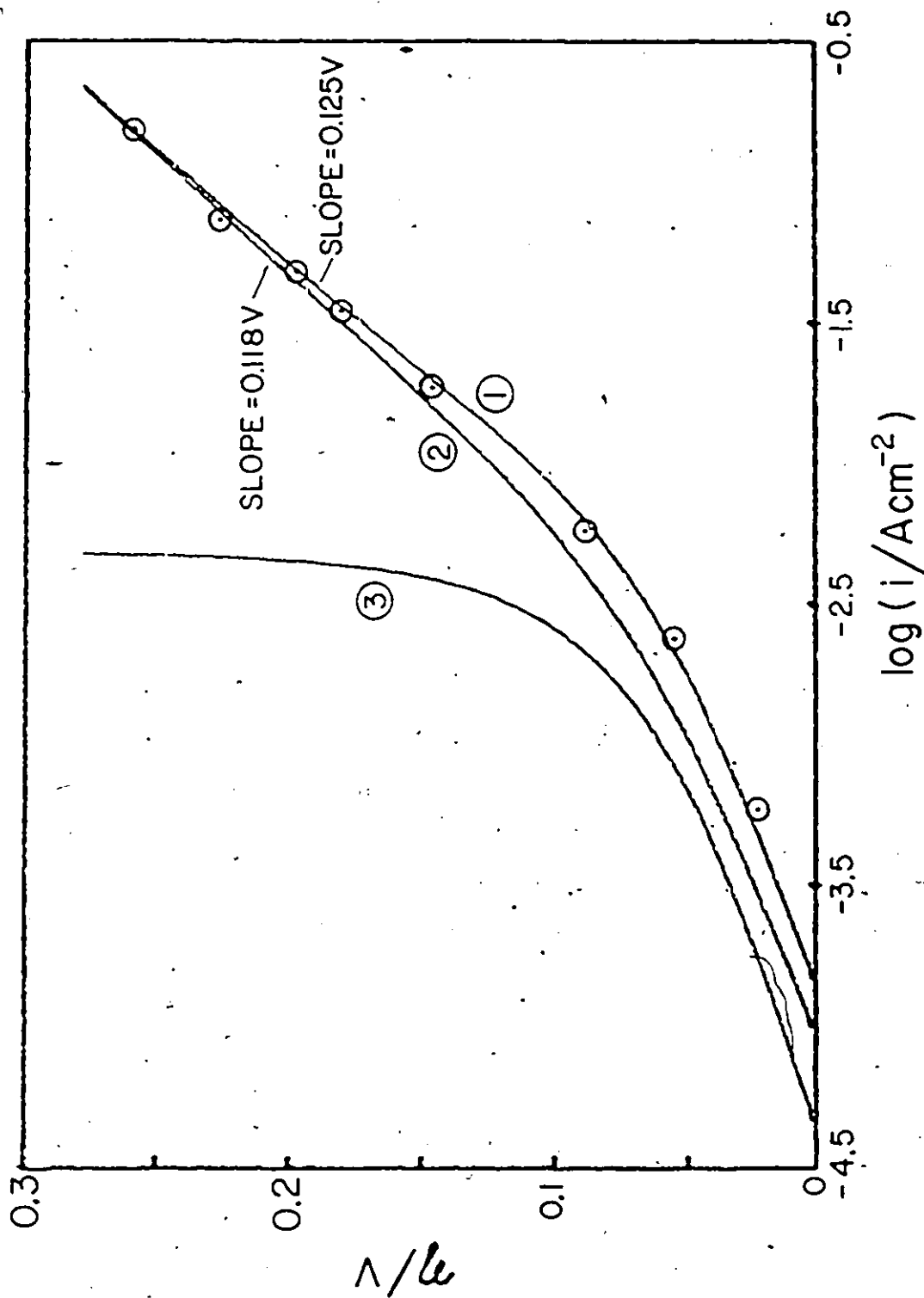


Fig. 4.25 Experimental (circled points) and simulated (solid line) Tafel plots for the h.e.r. at Ni-Mo-Cd plated electrode in 0.5 M NaOH at 296K. Solid lines represent simulated behavior using eqn. (4.19) with the same rate constants as in Fig. 4.23, but taking $k_4=0$ for line 2 and $k_2=0$ for line 3.

path 4 gives a greater and greater contribution to the total current-density as temperature raised, since more hydride is involved at high temperature giving a more significant low Tafel slope region as found from the potential decay and polarization experiments at high T (see section 4.1.1).

Fig. 4.26 show the calculated η vs C_ϕ plots, using the simulated rate constants and q_1 , q_2 parameters the same as in Fig. 4.23. In Fig. 4.26, curve 1 is the $C_{\phi,1}$ vs η plot, which corresponds to 2d-adsorbed o.p.d. H; curve 2 is the $C_{\phi,2}$ vs η plot, which it is thought corresponds to a 3d-adsorbed hydride species. The charge for "full" coverage of hydride (peak area of curve 2) is 10 times larger than that for 2d-adsorbed H (peak area of curve 1). The value of $q_2 = 50 \text{ mC cm}^{-2}$ suggests that the hydride phase is equivalent to ca. 2 layers of o.p.d. H, if we take the "roughness factor" = 100 which is estimated from the value of C_{dl} , and "one monolayer" charge = $250 \text{ } \mu\text{C cm}^{-2}$. We shall encounter this multi-layer o.p.d. H situation again in the case of the Pt electrode in acid solution (see section 4.3), where it is related to better electrocatalytic activity, i.e. low Tafel slope and high i_0 , than in alkaline solutions.

The shape of curve 2 in Fig. 4.26 and the magnitude of the C_ϕ values are similar to the behavior of the C_ϕ vs η relation determined by the potential decay method (see Fig. 4.8, curve for 296 K), though the C_ϕ vs η behavior in Fig. 4.8, determined by the potential decay method represents the sum of the C_{dl} , $C_{\phi,1}$ and $C_{\phi,2}$ ($C_{\phi,2} \gg C_{dl} + C_{\phi,1}$ in this case).

The simulated curves for the a.c. behavior of the Ni-Mo-Cd plated electrodes fit the experimental curves quite satisfactorily but not so well as for the results on Ni and on Pt (see below, section 4.3.2). This may be due to the complexity of the h.e.r. at this kind of electrode, especially with regard to the kinetical involve-

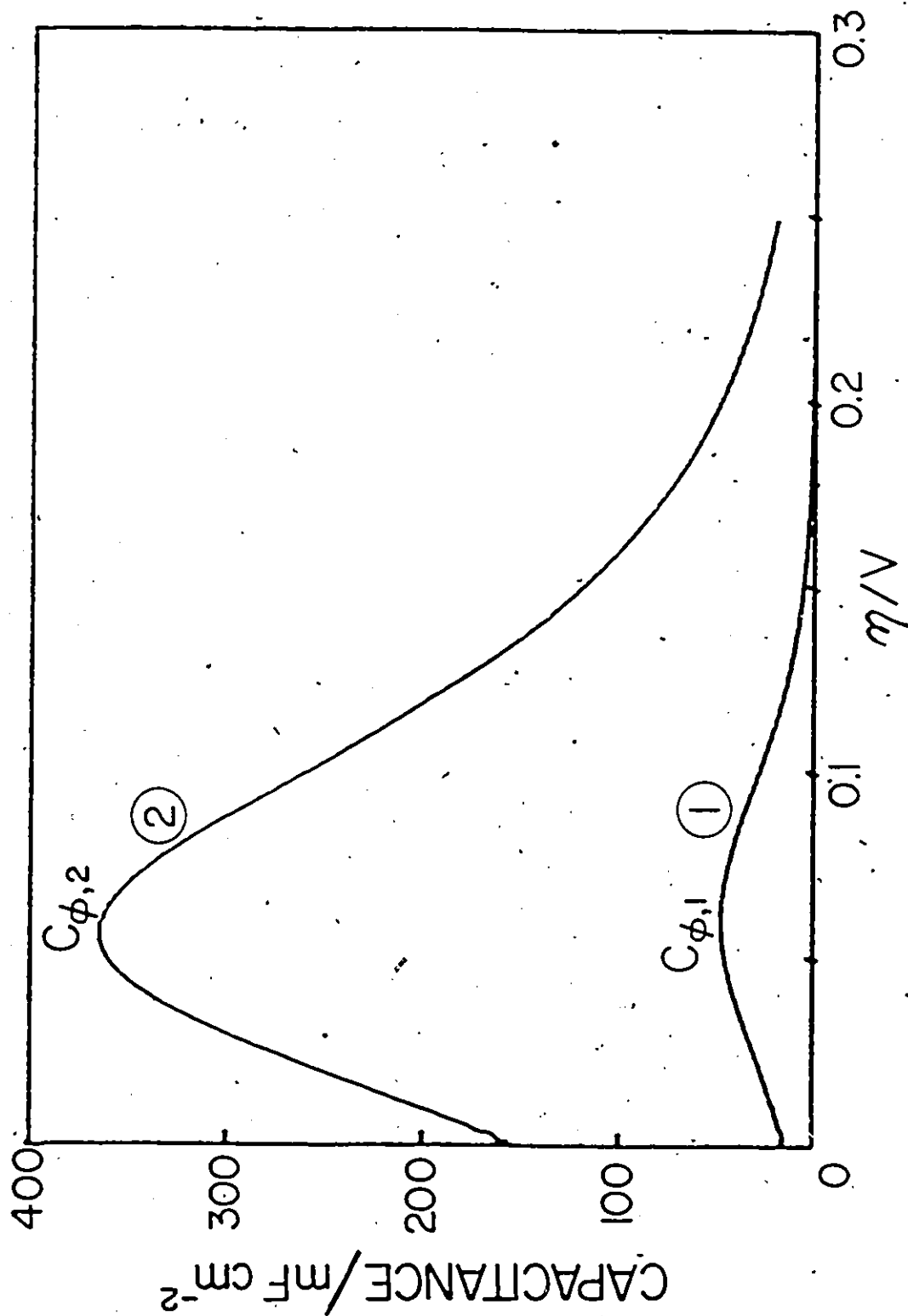


Fig. 4.26 Calculated η vs C_{ϕ} plots, using the simulated rate constants and q_1, q_2 parameters, ^{the} same as in Fig. 4.23. Curve 1 is $C_{\phi,1}$ vs η and Curve 2 is $C_{\phi,2}$ vs η plots.

ment of anhydride phase and the probability that the reaction model in diagram (4.17) is over-simplified. This model probably should include a) an equilibrium between the H sorbed in the 2d and 3d phases involving θ_1 and θ_2 values; b) the contributions of recombination-desorption in steps 2 and electrochemical-desorption in step 4 in diagram 4.17, which, of course, would lead to much more complex mathematical equations (which could not be solved by the present treatment).

However, it seems that involvement of an hydride phase in the h.e.r. at Ni-Mo-Cd plated electrodes is strongly indicated and its presence improves the electrocatalytic property for the h.e.r., relative to bulk Ni, giving low Tafel slope behavior probably by providing another, third, pathway through a recombination-desorption mechanism involving the 3d-sorbed H.

4.1.3 Interim conclusions

(i) The methods of analysis of digitally recorded potential decay transients and a.c. impedance spectra, coupled with kinetic information provided by the Tafel polarization behaviour, allows a complete and accurate evaluation to be made of the potential-dependence of H coverage under conditions where appreciable continuous Faradaic currents are passing; such information was not previously obtainable in an unambiguous way, e.g. from charging curves or cyclic-voltammetry measurements.

(ii) The experimental behaviour shows that the h.e.r. at Ni and Ni-Mo-Cd composite materials proceeds on a surface partially covered to a limiting extent by the adsorbed intermediate, H. Experimentally determinable limiting coverages are attained at ca.

-0.15 to -0.25 V, E_H , and are temperature dependent.

(iii) The situation in (ii) allows determination of the ratio of the rate-constants for the rate-controlling desorption step to that for the discharge-chemisorption step.

(iv) Good polarization performance of the Ni-Mo-Cd electro-coated cathodes arises, in part, from the low-slope region that persists increasingly to higher current densities as temperature is raised.

(v) The low-slope region is associated with a region of high H pseudocapacitance. A facile desorptive mechanism in H_2 evolution, involving this H species, which may be in the form of a surface phase hydride, is indicated.

(vi) The behaviour of the Ni-Mo-Cd coated electrodes differs in some important ways from metallic Ni and bulk Ni-Mo alloy, so the good performance of the first electrode material is not due simply to the large real-to-apparent areas that can be realized with coating procedures.

4.2 Au electrode

4.2.1 u.p.d. H at Au

It is well known^{100,169,170} that there is no detectable u.p.d. of H at Au electrode, as can be easily demonstrated in a CV experiment down to potentials near the H_2 reversible potential (contrast Pt, Rh and Ir). Fig. 4.27 shows the CV profiles for an Au electrode in 0.1 M H_2SO_4 (Fig. 4.27a) and 0.2M NaOH (Fig. 4.27b) at a sweep-rate 0.050 V s^{-1} , 296K. The peaks at the right-hand-side (at the high potential end) of the profile in Fig. 4.27 correspond to the well-known irreversible processes of formation and reduction of the surface oxide^{109-171,181-184}. At the left-hand-side of the profile ~~in~~ Fig. 4.27, down to the H_2 equilibrium potential, ca. 0.0V, no u.p.d. H peaks can be detected such as are clearly manifested at Pt electrodes^{100,150} over the potential range 0.05-0.4V, depending on pH and electrolyte composition. However, the CV experiment cannot indicate if significant o.p.d. H arises at potentials negative to the H_2 reversible potential where H_2 evolution currents are appreciable ($\log i_0$ for Au is ca. $10^{-6} \text{ A cm}^{-2}$).

While there is evidently no u.p.d. coverage of H at Au, the experimental behavior of possible o.p.d. H behavior at Au is still a matter of interest: a) inherently, in relation to the kinetics and involvement of adsorbed H in the h.e.r. at Au and b) to verify the potential decay treatment and expected behavior in a case where $\theta_H \ll 1$ and probably negligible over accessible ranges of η , as at Hg.

4.2.2 η vs $\log i$ and $\log(-dV/dt)$ relations

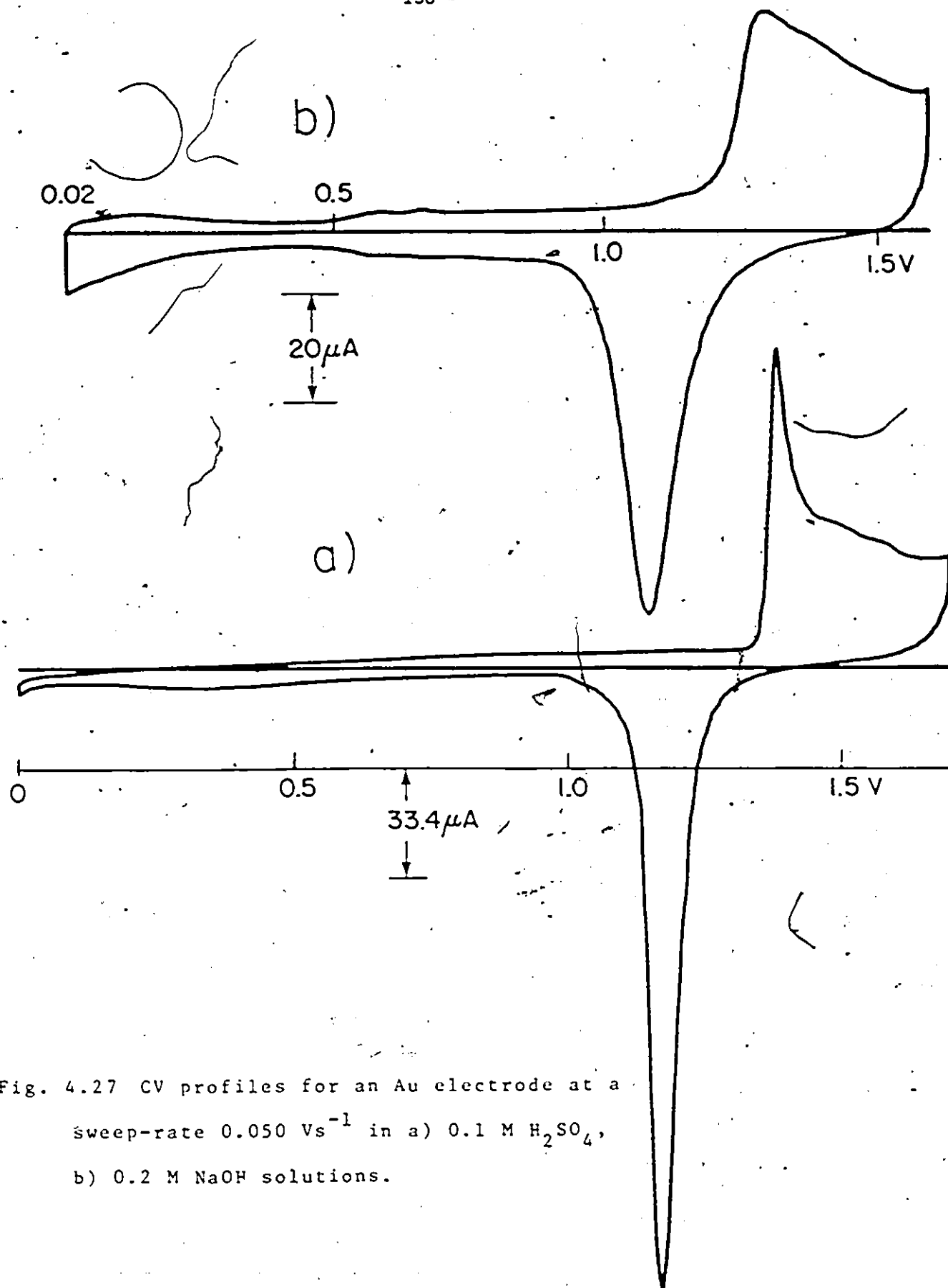


Fig. 4.27 CV profiles for an Au electrode at a sweep-rate 0.050 Vs^{-1} in a) $0.1 \text{ M H}_2\text{SO}_4$, b) 0.2 M NaOH solutions.

In relation to the u.p.d. H result from CV, it is of interest to determine if o.p.d. H is detectable at the Au electrode for the h.e.r. at this metal. Fig. 4.28 shows η vs $\log t$ plots in 0.2M NaOH solution at 296K for interruption of polarization at four current density values: (1) 0.6×10^{-3} , (2) 1.52×10^{-3} , (3) 2.25×10^{-3} and (4) $5.8 \times 10^{-3} \text{ A cm}^{-2}$, while Fig. 4.29 shows the η vs $\log (-dV/dt)$ relation for the same data as in Fig. 4.28. In contrast to the η against $\log t$ plots (Fig. 4.28), the plots of η against $\log (-dV/dt)$ (Fig. 4.29) are coincident for the four curves at their upper ends. Note that in these plots there is no arbitrariness involved, as there is unavoidably in plots such as those in Fig. 4.28 because of empirical evaluation of τ , as mentioned earlier in the cases of Ni and Ni-Mo-Cd electrodes. This difficulty is avoided by treating the data according to eqn. (3.13).

The curve 1 in Fig. 4.30 is the η vs $\log i$, Tafel plot for the h.e.r. in 0.2M NaOH at 296K, while curve 2 in Fig. 4.30, as a comparison, represents the η vs $\log (-dV/dt)$ data, the same as does curve 4 in Fig. 4.29. The two curves in Fig. 4.30 are two almost parallel straight lines (in the range of five decades of current density and 0.5V of potential!) with slopes equal to 0.12 V separated by a distance between the lines equal to 1.35 on the log scale (1 in units of mA cm^{-2}). The parallel relation between these two plots (see eqn. 3.14) indicates that only a constant capacitance is involved at the electrode/solution interphase. From the eqn. (3.14) it is evident that $\log C (\text{mF cm}^{-2}) = -1.35$, so that the value of the capacitance is $45 \mu\text{F cm}^{-2}$, which is reasonably close

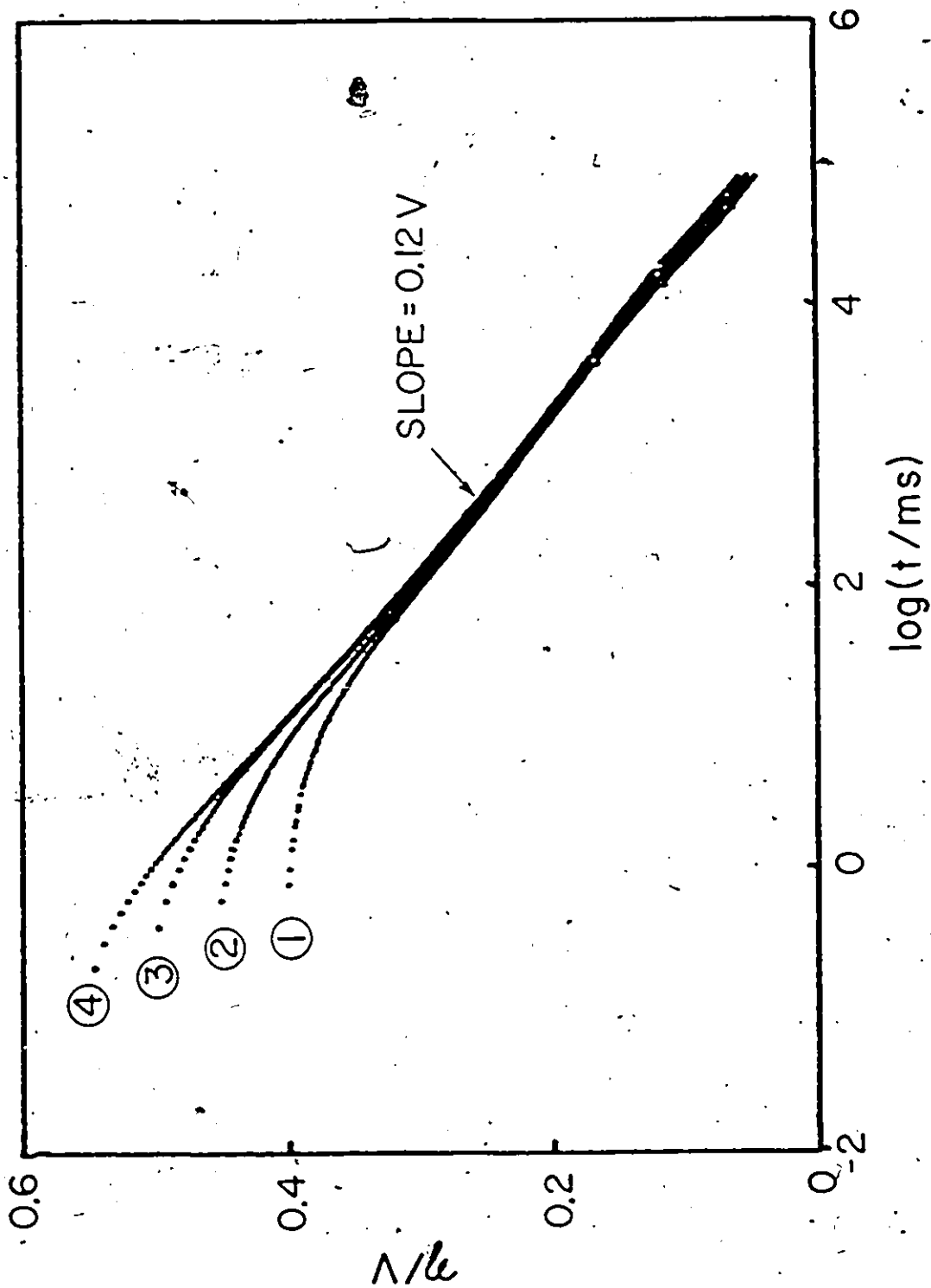


Fig. 4.28 Plots of η vs $\log t$ in 0.2 M NaOH solution at 296K for interruption of polarization at four current density values: (1) 0.6×10^{-3} ; (2) 1.52×10^{-3} ; (3) 2.25×10^{-3} and (4) $5.8 \times 10^{-3} \text{ A cm}^{-2}$.

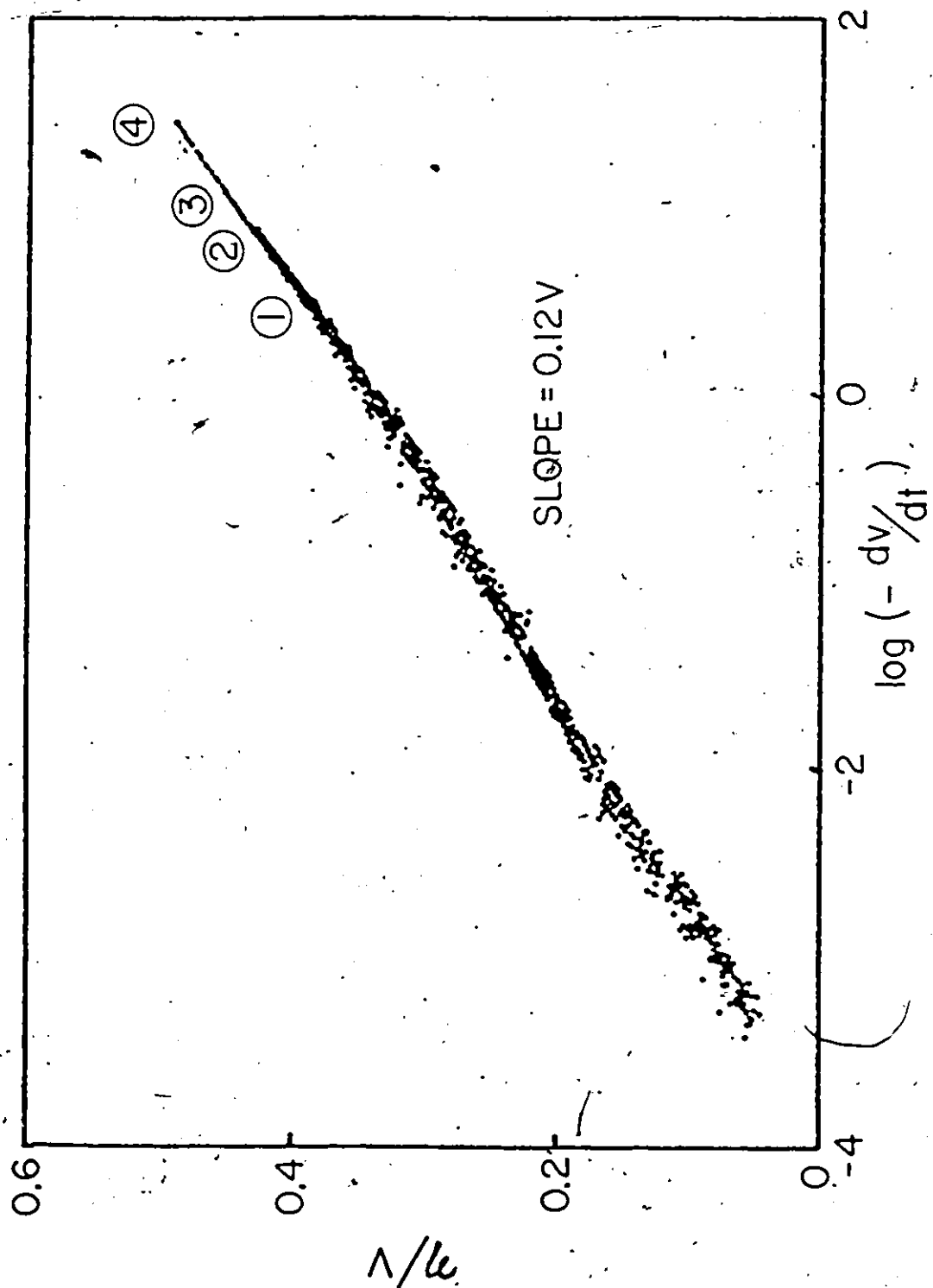


Fig. 4.29 Plots of η vs $\log(-dv/dt)$ for the same data as in Fig. 4.28.

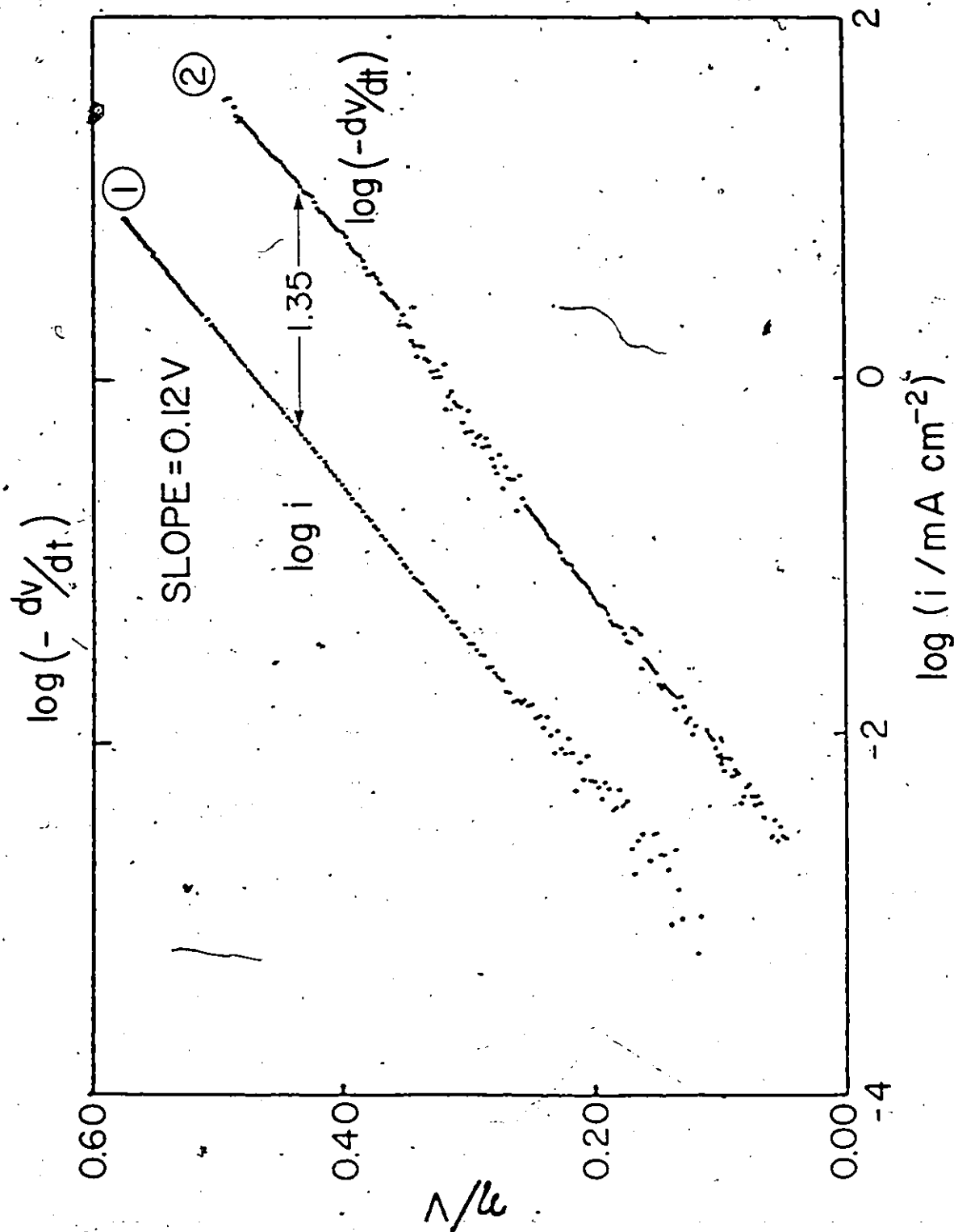


Fig. 4.30 Tafel plot for the h.e.r. in 0.2N NaOH at 296K (curve 1) and vs $\log(-dv/dt)$ plot using the same data as for curve 4 in Fig. 4.29.

to what may be expected for C_{dl} at Au.

Fig. 4.31 shows η vs $\log i$ plots in 0.1M H_2SO_4 solution at 296K at two initial current density values: (1) 3.68×10^{-3} , (2) $6.1 \times 10^{-3} A cm^{-2}$. In Fig. 4.32 curve 1 is the Tafel plot and curve 2 is the η vs $\log(dV/dt)$ plot for the same solution as in Fig. 4.31. The two curves in Fig. 4.32 are also two parallel but curved lines, which become straight at $\eta > 0.05V$ with slopes equal to ca. 0.060V and a separation distance equal to 1.68 on the log scale (i in units of $mA cm^{-2}$). As discussed above, parallel lines in these plots imply constant capacitance and the value 1.68 corresponds to a value of capacitance of 21 $\mu F cm^{-2}$ in this case which can reasonably be assigned to C_{dl} . Note that the value of C_{dl} is twice times larger in alkaline solution compared with the acidic solution (the same situation is observed at un-activated Pt electrodes as well; see section 4.3.2.4). This difference is probably due to anion (HSO_4^-) adsorption in the case of the acidic solution, giving rise to a lower compact double-layer capacitance. Similar behavior follows from the CV profiles (Fig. 4.27).

4.2.3 Capacitance behavior of o.p.d. H and the reaction mechanisms

The C vs η plots for alkaline solution treated using eqn. (3.13) and the data in Fig. 4.29 is shown in Fig. 4.33(a). Only a very small C_0 contribution can be observed in Fig. 4.33(a), which gives o.p.d. H coverage, θ_H , less than 0.05 at $\eta = 0.3V$. According to the discussion in section 1.6.2, the r.d.s. is therefore probably the discharge process (eqn. 1.6) corresponding to a Tafel slope 0.120V with rather small θ_H (close to 0).

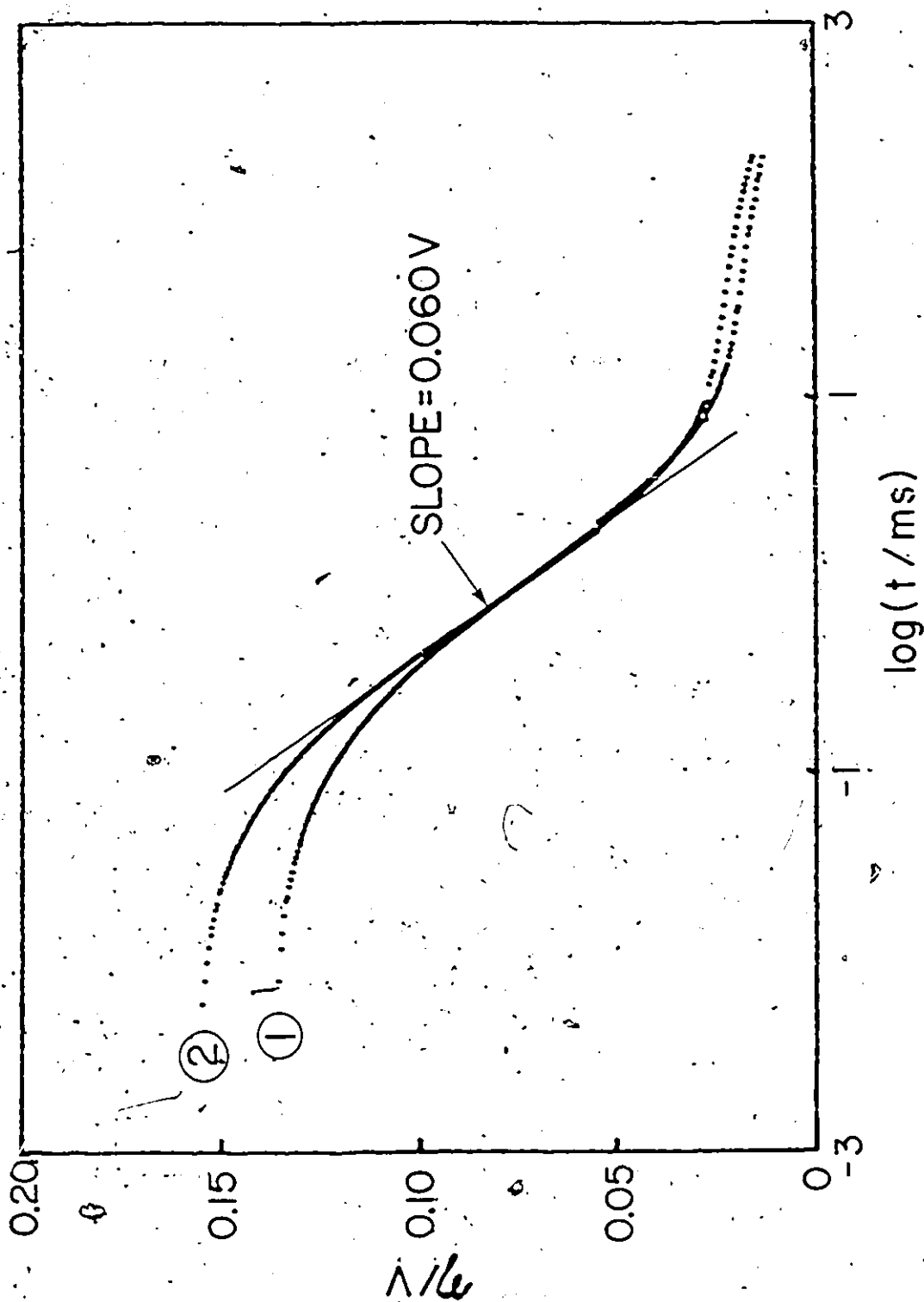


Fig. 4.31 Plots of j vs $\log t$ for the h.e.r. at Au electrode in 0.1 M H_2SO_4 solution at 296K, at two initial current density values: (1) 3.68×10^{-3} ; (2) $6 \times 10^{-3} \text{ A cm}^{-2}$.

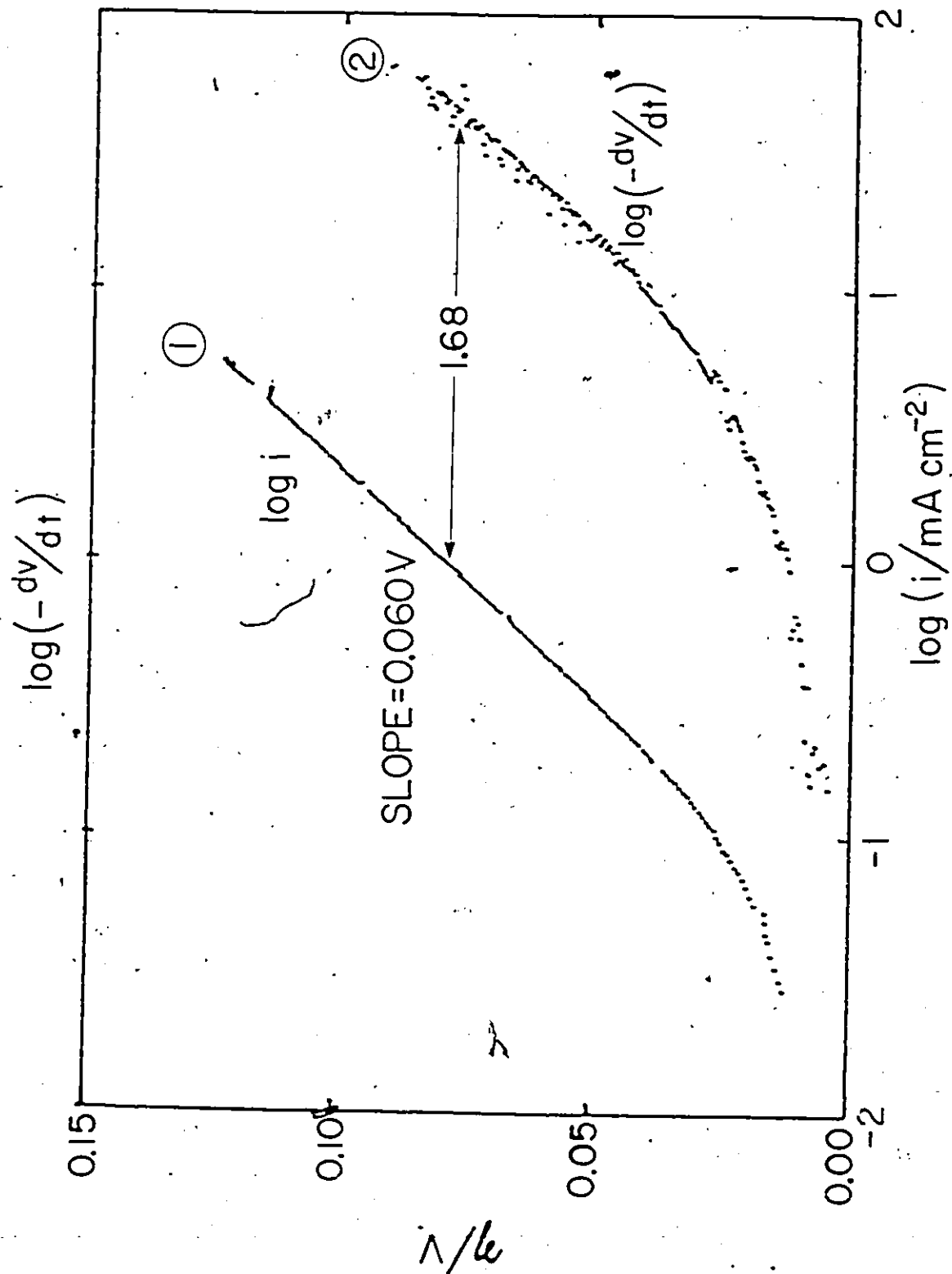


FIG. 4.32 Tafel plot and η vs $\log(-dv/dt)$ plot for the same conditions as in Fig. 4.31.

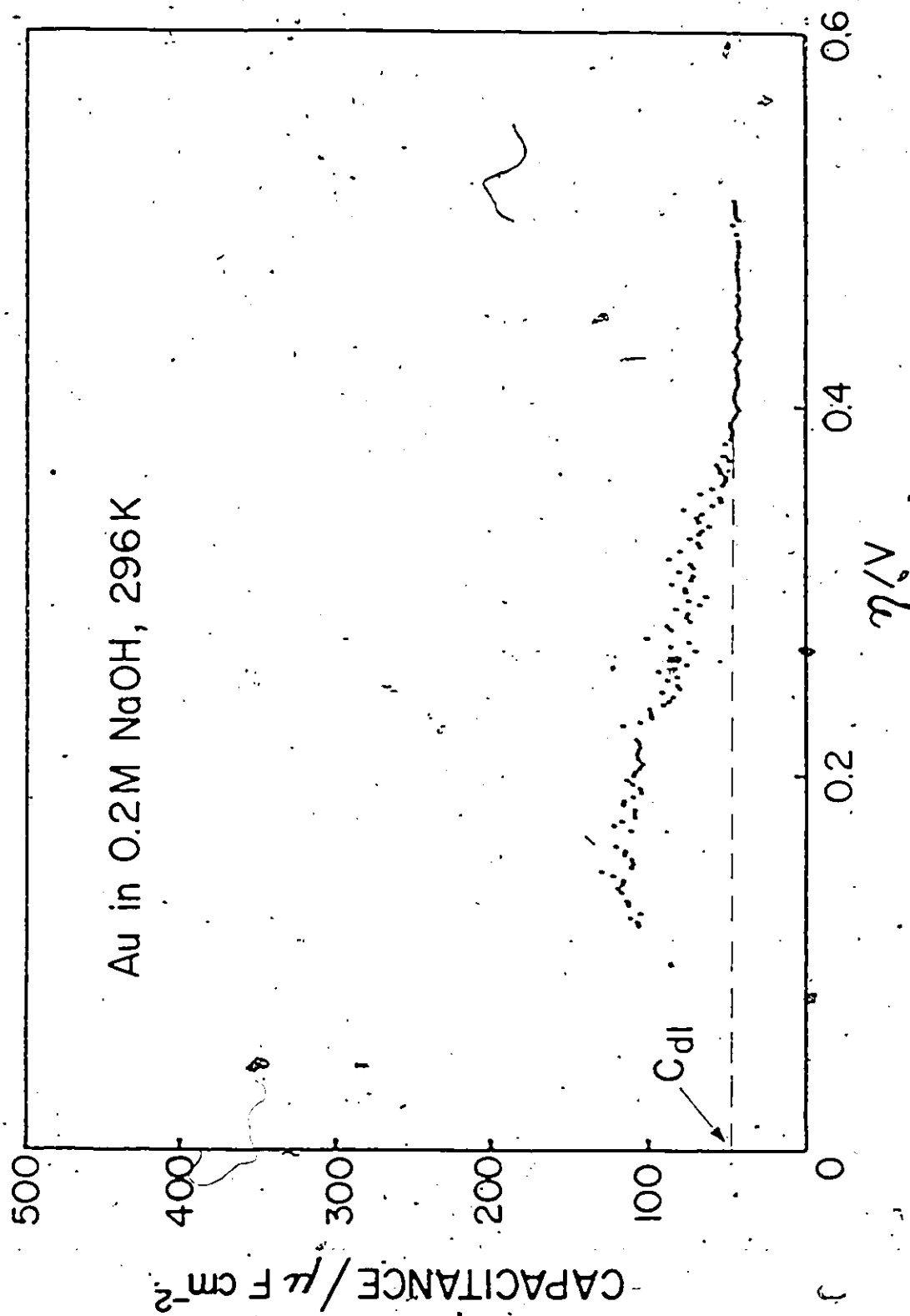


FIG. 4.33(a) Capacitance C vs η plots for the h.e.r. at Au electrode in 0.2M NaOH solution.

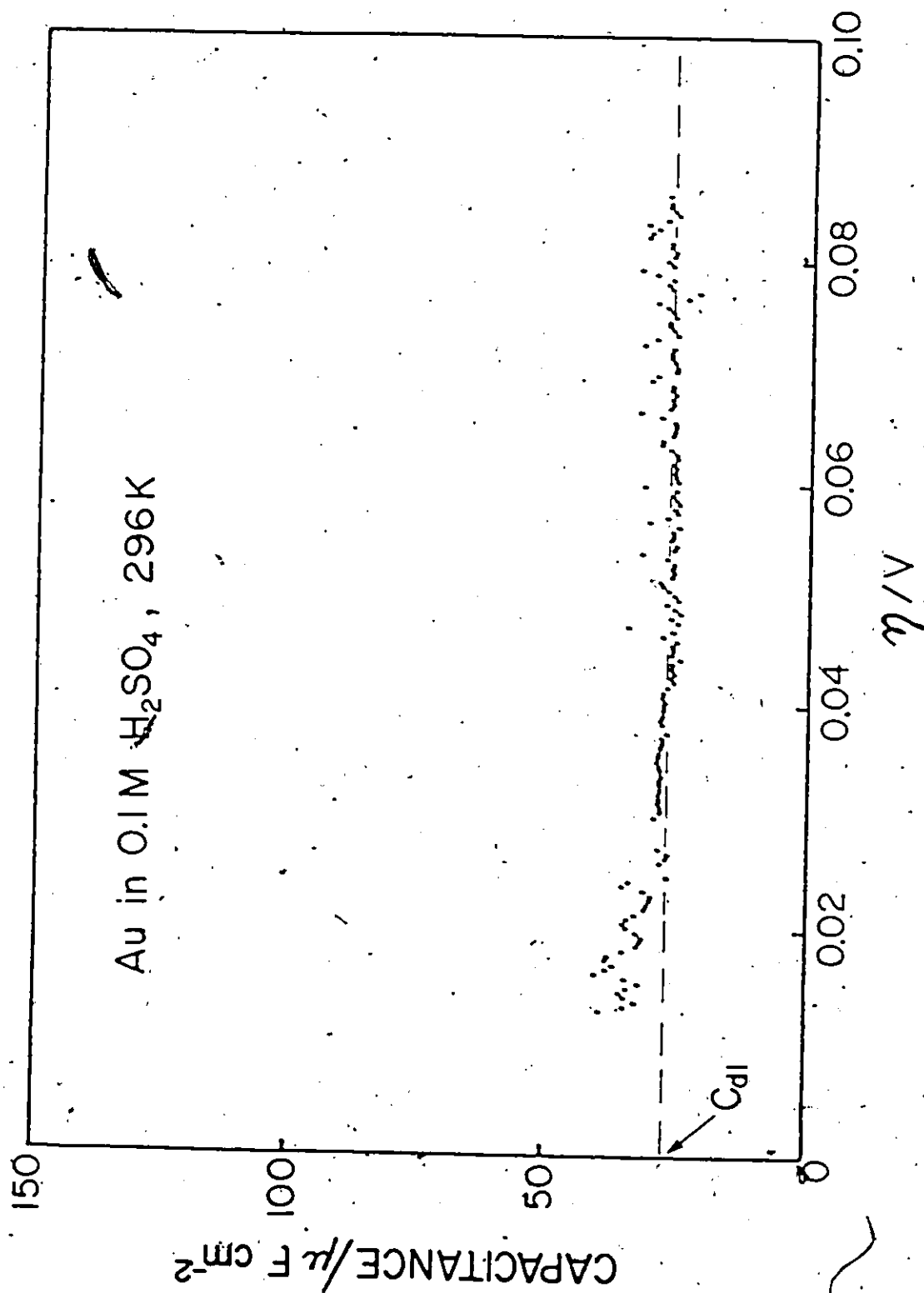
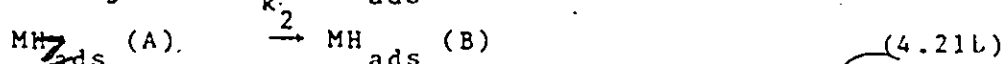
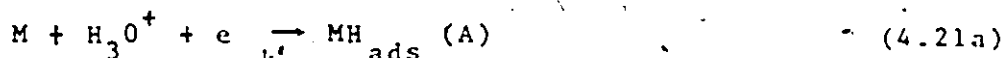


Fig. 4.33(b) Capacitance C vs η plots for the h.e.r. at Au electrode in 0.1 M H_2SO_4 solution.

The C vs η plot for acidic solution, treated using eqn. (3.13) and the data in Fig. 4.32, is shown in Fig. 4.33(b). Only the double-layer capacitance, C_{dl} , can be determined, which is a constant value (ca. $21 \mu F \text{ cm}^{-2}$) in the potential range studied.

The rather unusual Tafel slope value, equal to $0.060V$, ($-2.3RT/F$), has been discussed in previous work by Bockris et al.¹⁷², who attributed it to a "surface diffusion" rate controlling process, prior to desorptive discharge at active sites:



that is, the rate determining step (eqn. 4.21b above) is the migration of H atoms from some point (A) on the electrode at which they are discharged, either a) to meet another H atom at site (B) "chemical-recombination" to form a H_2 or b) to move to some active place (B) where "electrochemical-desorption" to form H_2 can take place.

For this situation, the Langmuir quasi-equilibrium assumption (see section 1.5.2) can reasonably be applied with θ_H close to zero (eqn. 1.11). The rate of the reaction may then be written:

$$i = k'_2 \theta_H = k'_2 K_1 \exp(\eta F/RT) \quad (4.22)$$

Thus, a Tafel slope $b = d\eta/d\log i = 2.3RT/F = 0.059V$ results at $T = 298$, with no barrier symmetry factor being then involved.

The slow surface diffusion may arise in aq. H_2SO_4 solutions on account of the known¹⁶⁹ very strong adsorption of HSC_4^- or SO_4^{2-} ions, despite the potential of the h.e.r. region being some

0.7V negative to the potential of zero charge of Au.

4.2.4 Interim conclusion for Au electrode

As with u.p.d. of H at Au, also no o.p.d. H can be detected at Au electrodes either in acidic or alkaline solutions at 296K, i.e. the h.e.r. proceeds at the almost bare Au surface, apart from the presence of H_2O dipoles and possibly adsorbed anions in acidic (H_2SO_4) solution. In alkaline solution, the reaction is controlled by the discharge step with θ_H close to zero. In acidic solution, the reaction is characterized by a rate-controlling "surface diffusion" process.

4.3 Bright Pt disc electrode

4.3.1 (1) Potential decay method

Derivation of information on coverage and pseudocapacitance of o.p.d. H requires the complementary measurement of polarization ($i(\eta)$) behaviour and the potential relaxation. These aspects will be reported here sequentially in the two sections which follow.

4.3.1.1 log(current-density) vs Potential Relations

(a) Acidic solutions

We first show the Tafel relations for the Pt electrode in acid solutions in order to characterize the polarization behaviour and thus evaluate C_ϕ as $f(\eta)$ through eqn. (3.13). Fig. 4.34 shows the η vs i plots (corrected for the back-reaction current component according to the H recombination mechanism*) for a Pt electrode at a rotation rate of 3600 rpm** in 0.5 M aq. H_2SO_4 solution. Note, however, that analysis of the potential decay measurements to obtain $C_{dl} + C_\phi$ does not require correction of the measured currents since it is the net, experimentally recorded $i(\eta)$ value that determines dn/dt at a given η .

Curve 1 in Fig. 4.34 represents the Tafel plot for an anodically activated Pt electrode; the relation exhibits a linear region with a slope of 0.036 V at low η while the slope increases with η as $\eta > \text{ca. } 0.05$ V. Curves 2, 3 and 4 are Tafel plots for the electrode initially activated (as with curve 1) but cathodically polarized to $\eta = 0.050$ V for durations of 15, 30 and 60 minutes,

*Although it is proposed in this section that the pathway involves two parallel steps, recombination and electrochemical-desorption, the recombination step always makes the major contribution to the reaction rate at low η and the back-reaction is also only significant at low η .

** As mentioned in section 2.2.1, the experiments described here were conducted at a Pt RDE in order to eliminate H_2 supersaturation and diffusion effects, and stagnant bubble formation.

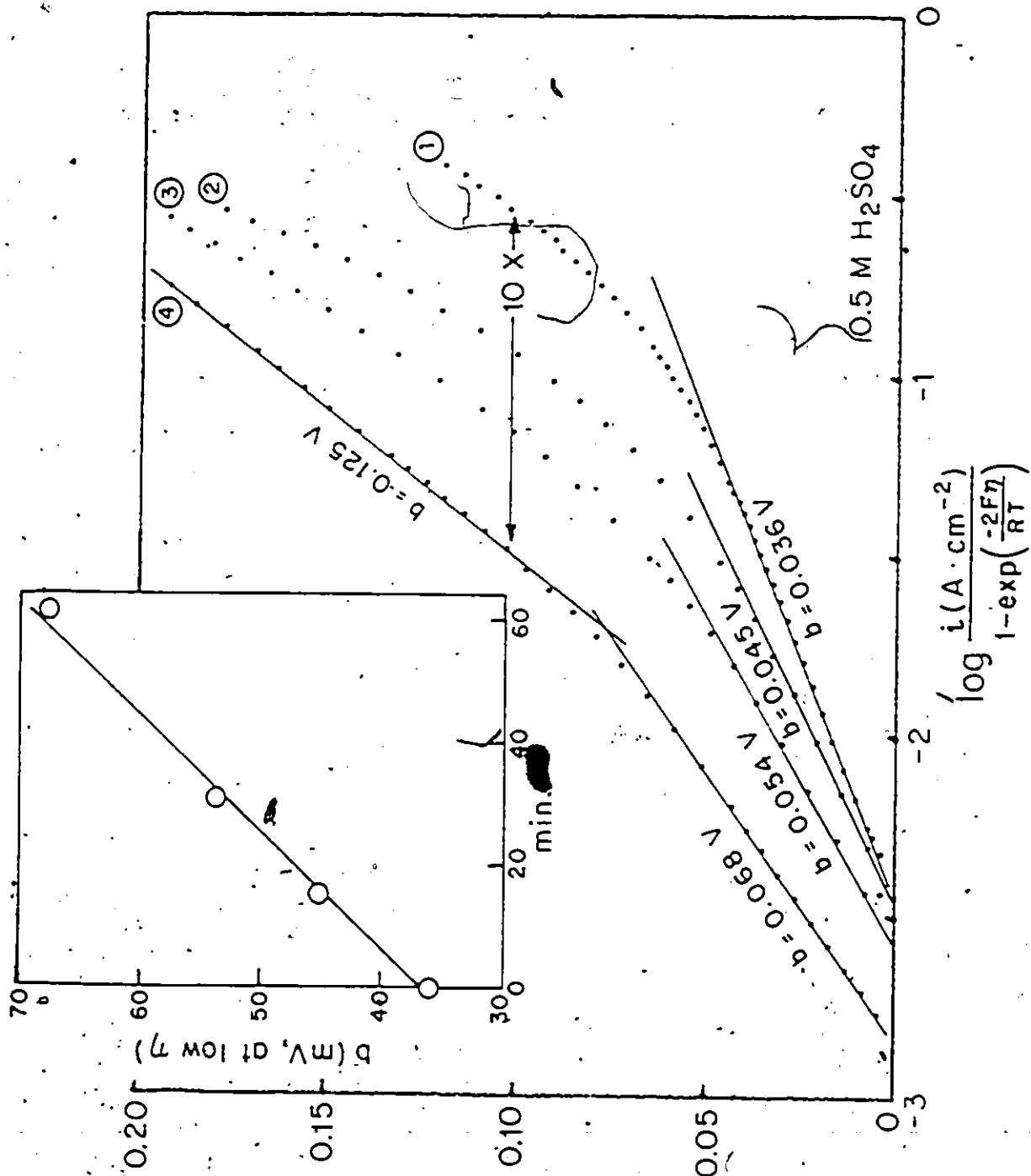


Fig. 4.34 Tafel plots, corrected for back reaction current, for the h.e.r. on a Pt disc electrode at a rotation rate of 3600 r.p.m. in 0.5 M H_2SO_4 at 296K, for different electrode pretreatments: 1) anodically activated; others after cathodic polarizations at $\eta = 0.050$ V for 2) 15; 3) 30 and 4) 60 min. Inset figure: Tafel slopes of linear region at low η : plot of b vs cathodic polarization time.

respectively. Through curves 1 to 4, the slopes of the linear regions at low η increase from 0.036 V to 0.068 V linearly with time (as shown in Fig. 4.34, inset).

It is seen that when $\eta > \text{ca. } 0.075 \text{ V}$, the Tafel relation becomes a straight line with slope equal to 0.125 V (upper region of curve 4 in Fig. 4.34). This implies (cf. refs, 22,24) that the rate controlling step is electrochemical-desorption with $\theta_H \rightarrow 1$ or the initial discharge step, with $\theta_H \rightarrow 0$. Fig. 4.34 shows that the Pt electrode becomes a poorer electrocatalyst for the h.e.r. as the cathodic polarization time increases, as also known from other work^{70,82,173}.

From Fig. 4.34 the exchange current-density, i_0 , is $3.2 \times 10^{-3} \text{ A cm}^{-2}$ for the anodically activated electrode and $1.6 \times 10^{-3} \text{ A cm}^{-2}$ for the electrode aged under polarization for 60 min., respectively. Comparing the curve 1 and curve 4, it is seen that the i_0 value for the activated electrode is only twice that for the aged electrode. However, the current-density i for the activated electrode is 10 times greater than that for an electrode aged for the same time at $\eta = \text{ca. } 0.1 \text{ V}$. This suggests that the difference between activated and aged electrodes is not only that they have different "active sites" or reaction surface area, but also that they exhibit a different potential dependence of the reaction rate and thus probably have different reaction mechanisms, or variably mixed mechanisms. Here it is also useful to point out that the practical electrocatalytic activity of an electrode is not to be measured just by its " i_0 value" but rather by the combination of i_0 and Tafel b parameters for the given process, as mentioned on p. 14.

(b) Alkaline solutions

Fig. 4.35 shows the η vs i plots for the Pt rotating disc

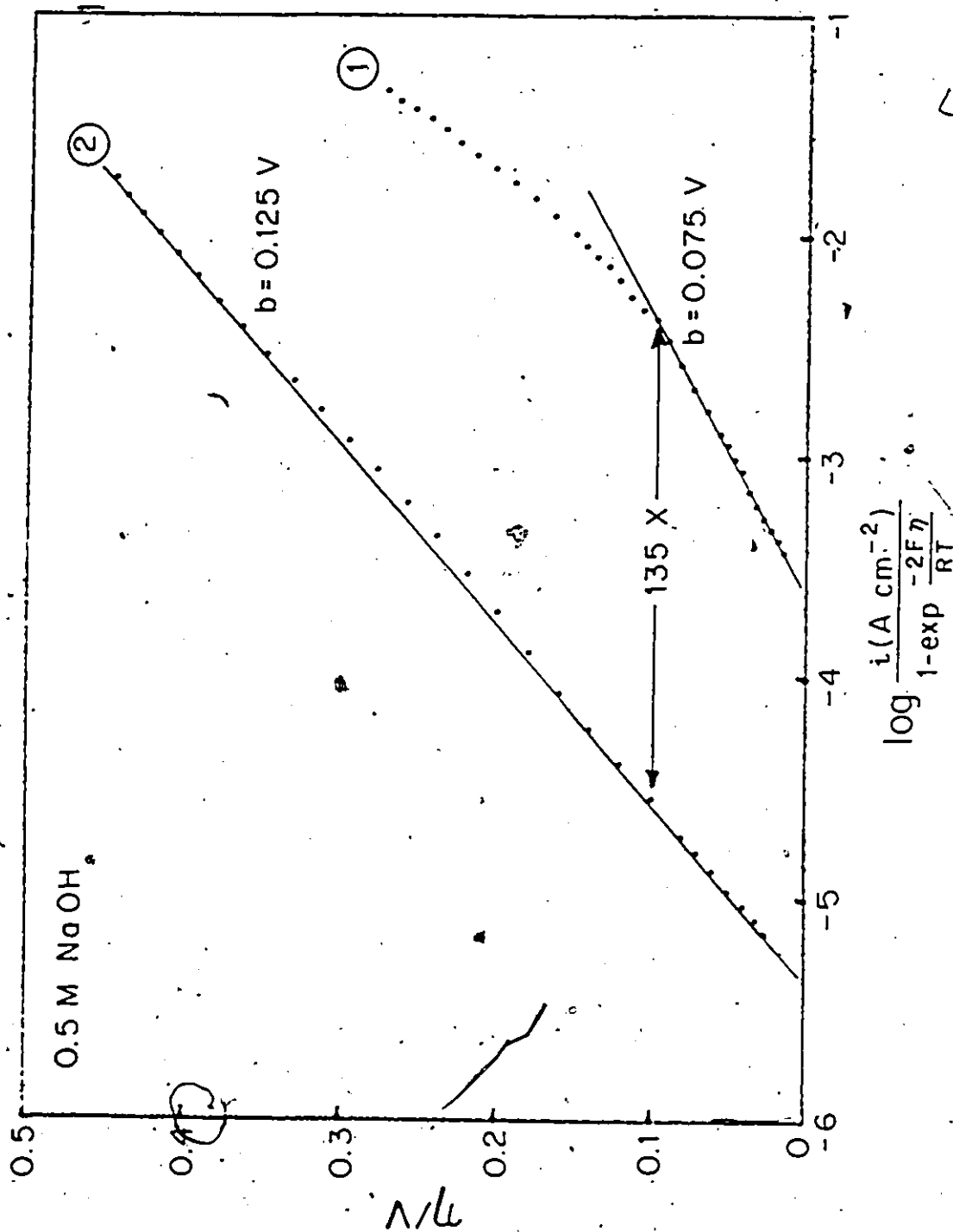


Fig. 4.35 Tafel plots, corrected for back reaction current, for the h.e.r. on a Pt electrode at a rotation rate of 3600 r.p.m. in 0.5 M NaOH at 296K, for different electrode pretreatments: 1) anodically activated; 2) after cathodic polarization at $\eta = 0.050 \text{ V}$ for 30 min.

electrode at a rotation rate of 3600 rpm in 0.5 M aq. NaOH solution.

Curve 1 in Fig. 4.35 which is the Tafel plot for an anodically activated electrode, exhibits a linear region with a slope of 0.075 V for $\eta < \text{ca. } 0.1$ V but with curvature beyond $\eta = \text{ca. } 0.1$ V.

Curve 2 in Fig. 4.35 is the Tafel plot for the same Pt electrode after 30 min. cathodic polarization at $\eta = \text{ca. } 0.050$ V and is a straight line with a slope of 0.125 V throughout the potential range measured. Curve 2 implies that the r.d.s. at an aged electrode in alkaline solution is either the electrochemical-desorption step with o.p.d. $\theta_H \rightarrow 1$ or the initial discharge step with o.p.d. $\theta_H \rightarrow 0$. We shall see below that the analysis of the potential decay measurements is able to define which of these conditions applies.

The decrease of activity of the Pt electrode with time in alkaline solution is appreciably more rapid than in acid solution. Fig. 4.35 shows that the current-density for the h.e.r. at the Pt electrode aged for 30 min. at $\eta = 0.050$ V becomes 135 times smaller than that for an activated electrode at the same potential. Fig. 4.35 indicates that the i_0 value for the activated Pt electrode in 0.5 M NaOH at 296 K is $3.1 \times 10^{-4} \text{ A cm}^{-2}$ which is actually greater than the literature reported datum, $8.7 \times 10^{-5} \text{ A cm}^{-2}$ 174.

4.3.1.2 Potential-Decay Behaviour

(a). Acidic solutions

The digitally acquired, potential relaxation data are shown as $f(\log t)$ in Fig. 4.36 and as $f(\log -dn/dt)$ in Fig. 4.37 for activated and aged Pt electrodes in 0.5 M H_2SO_4 . In both Figs. 4.36 and 4.37, curve 1 is for the anodically activated Pt electrode while curves 2, 3 and 4 are for the aged electrodes, i.e. after

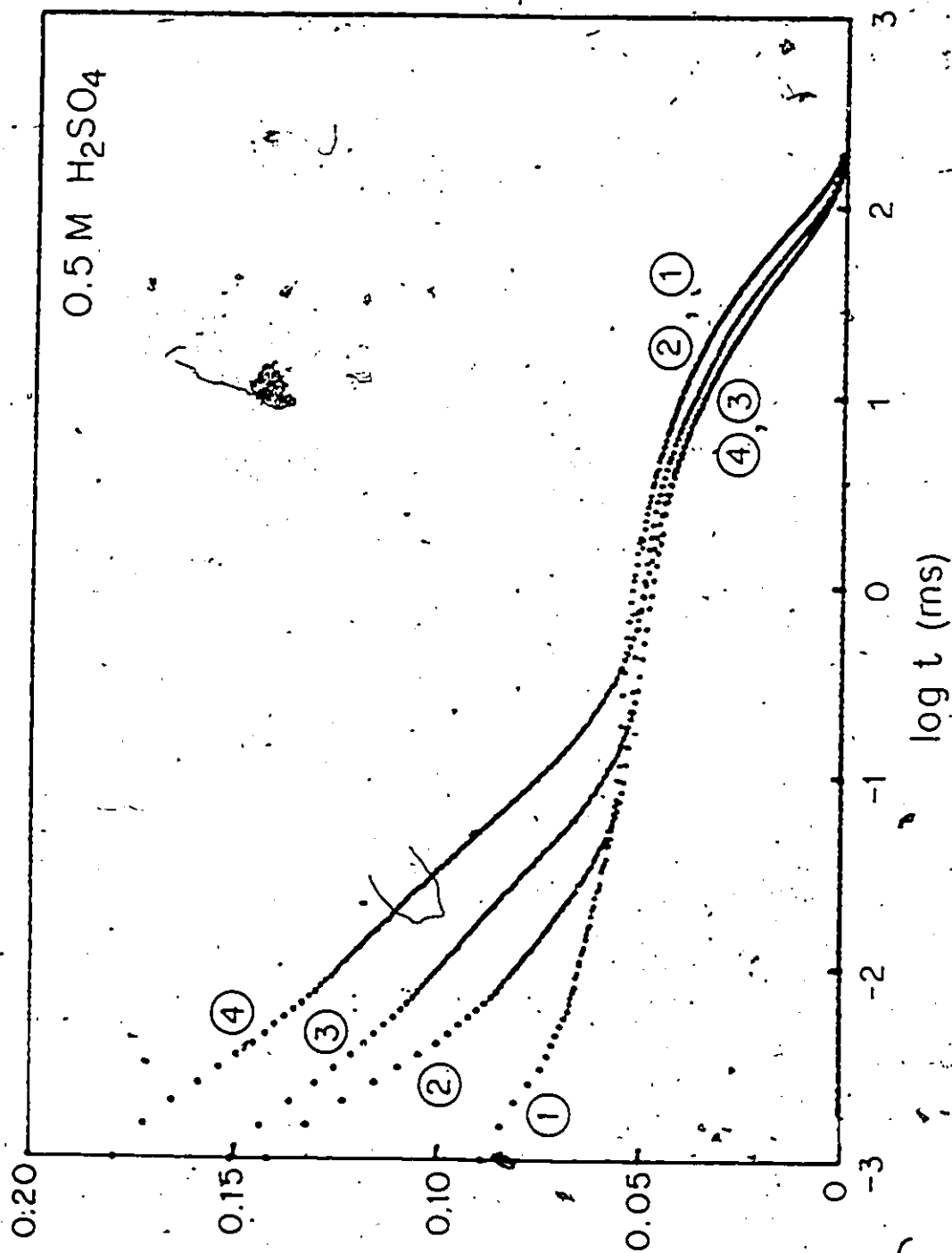


Fig. 4.36 Potential-decay plots for the h.e.r. at Pt at a rotation rate of 3600 r.p.m. in 0.5 M H₂SO₄ at 296K, for different pretreatments (corresponding to Fig. 4.34): 1) anodically activated; 2) after cathodic polarization at $\eta = 0.050$ V for 2) 15; 3) 30 and 4) 60 min.

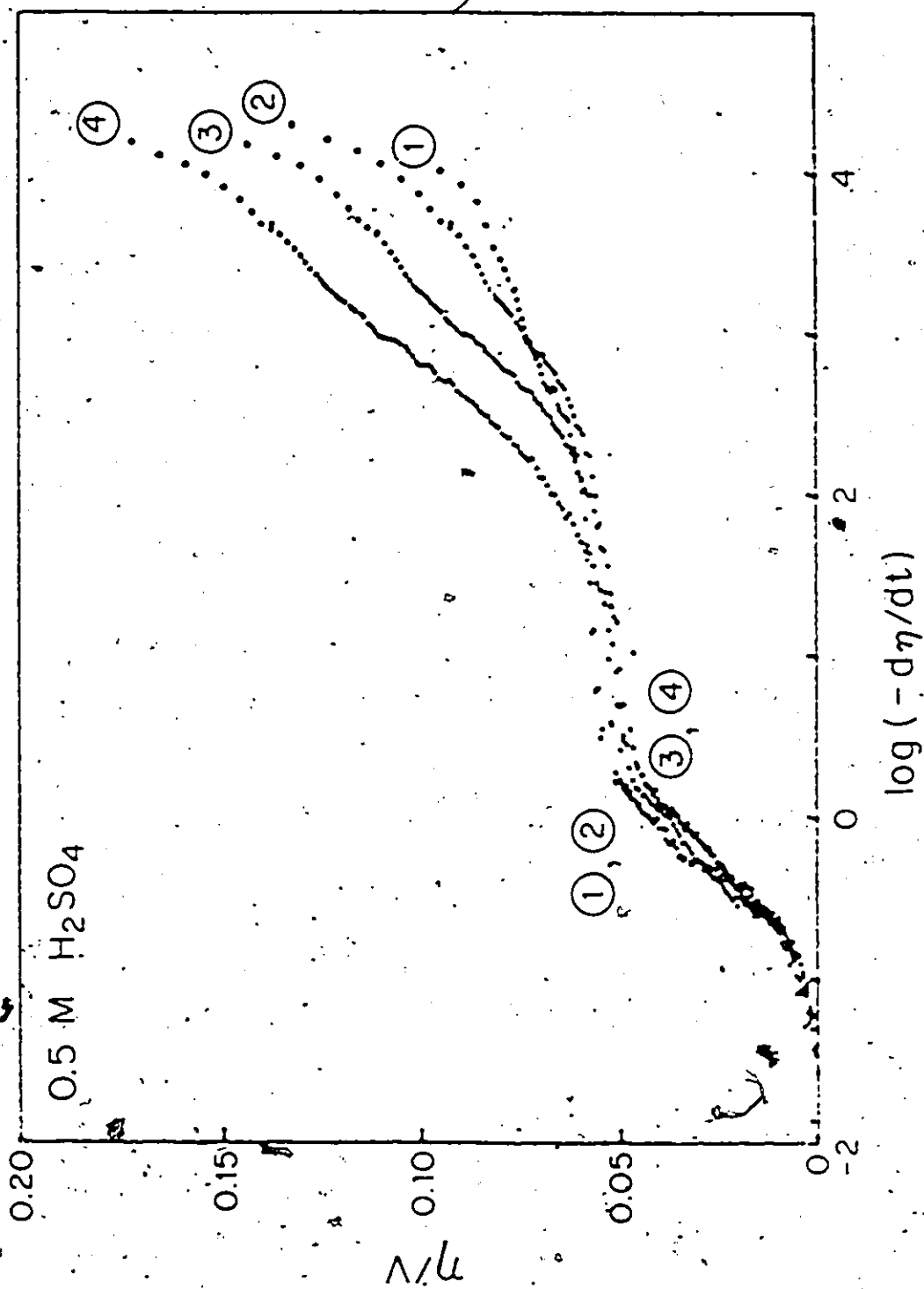


Fig. 4.37 Plots of η/c vs $\log(-d\eta/dt)$ for the same data as shown in Fig. 4.36.

cathodic polarization at $\eta = \text{ca. } 0.05 \text{ V}$ for 15, 30 and 60 min., respectively. These conditions correspond to those for the steady-state polarization relations shown in Fig. 4.34.

Fig. 4.36 shows (as is also apparent in Fig. 4.37) that the potential-decay curves have three principal regions: the first region arises when $\eta > 0.060 \text{ V}$, i.e. for times in the range 1 μs to ca. 0.3 ms ($\log t \text{ (ms)} = -0.5$), and corresponds^{133,175} to discharge of the double-layer capacitance through the non-linear Faradaic reaction resistance¹³⁴⁻¹³⁷. The third region arises when $\eta > 0.060 \text{ V}$, for time in the range ca. 3 ms ($\log t \text{ (ms)} = 0.5$) to 160 ms ($\log t \text{ (ms)} = 2.2$) and corresponds to discharge of the o.p.d. H pseudocapacitance. The second region is a flat, intermediate one between the first and the third regions around $\eta = 0.060 \text{ V}$, over the time range ca. 0.3 ms to 3 ms. The total potential decay processes take only less than 0.2 s in acid at the Pt electrode, i.e. for the potential to decay to within 5 mV of the reversible potential.

We know from previous works^{38,103} that C_ϕ is a $f(\eta)$ and, for Ni and Ni-Mo (section 4.1) alloys, is only significant at low overpotentials, reaching zero rapidly with increasing η , assuming a small or zero interaction factor¹⁰³. Since the Faradic reaction resistance corresponding to the high i_0 value, is relatively small for the h.e.r. at Pt, the discharge of the double-layer capacitance is almost complete when overpotentials are $> 0.060 \text{ V}$, within a very short time, since the H pseudocapacitance is still not yet significant at that potential; thus, it is possible to observe the flat intermediate second region of the potential-decay curves, as in Fig. 4.36.

Since the Faradaic reaction resistance becomes larger for the aged electrodes, the discharging time for C_{d1} (the first region) becomes increased as the duration of cathodic polarization is increased, due to the deactivating effect of impurities (see section 4.3.1.7).

In the work on the h.e.r. at Ni and Ni-Mo-Cd plated electrodes (section 4.1) in alkaline solution, only two principal linear regions were observed in the potential-decay relation, which indicated that only the region where overlapping discharge of C_{d1} and C_ϕ takes place, is observed; in those cases, the total times for the potential-decay processes to take place were ca. 10 s for Ni and 100 s for Ni-Mo-Cd plated electrodes, respectively.

(b) Alkaline solutions

Fig. 4.38 shows the η vs $\log t$ and Fig. 4.39 the η vs $\log(-d\eta/dt)$ plots for five initial polarization current-densities at an activated Pt electrode in 0.5 M aq. NaOH. As in the case of Ni and Ni-Mo-Cd alloy electrodes, two principal decay regions were now observed. As was discussed previously (section 3.1), V or η is strictly only a linear function in $\ln(t+\tau)$ [see eqn. (3.6)] as $C_\phi = 0$ or constant; therefore, when $t < \tau$, the relation between V and $\ln t$ will depend on the initial current, i ($\tau = bC_{d1}/i$) (see Fig. 4.38). However, in the η vs $\log(-d\eta/dt)$ plots, the five lines are found to be coincident, even up to high η values, because no arbitrary or empirical choice of τ is involved (see Fig. 4.39).

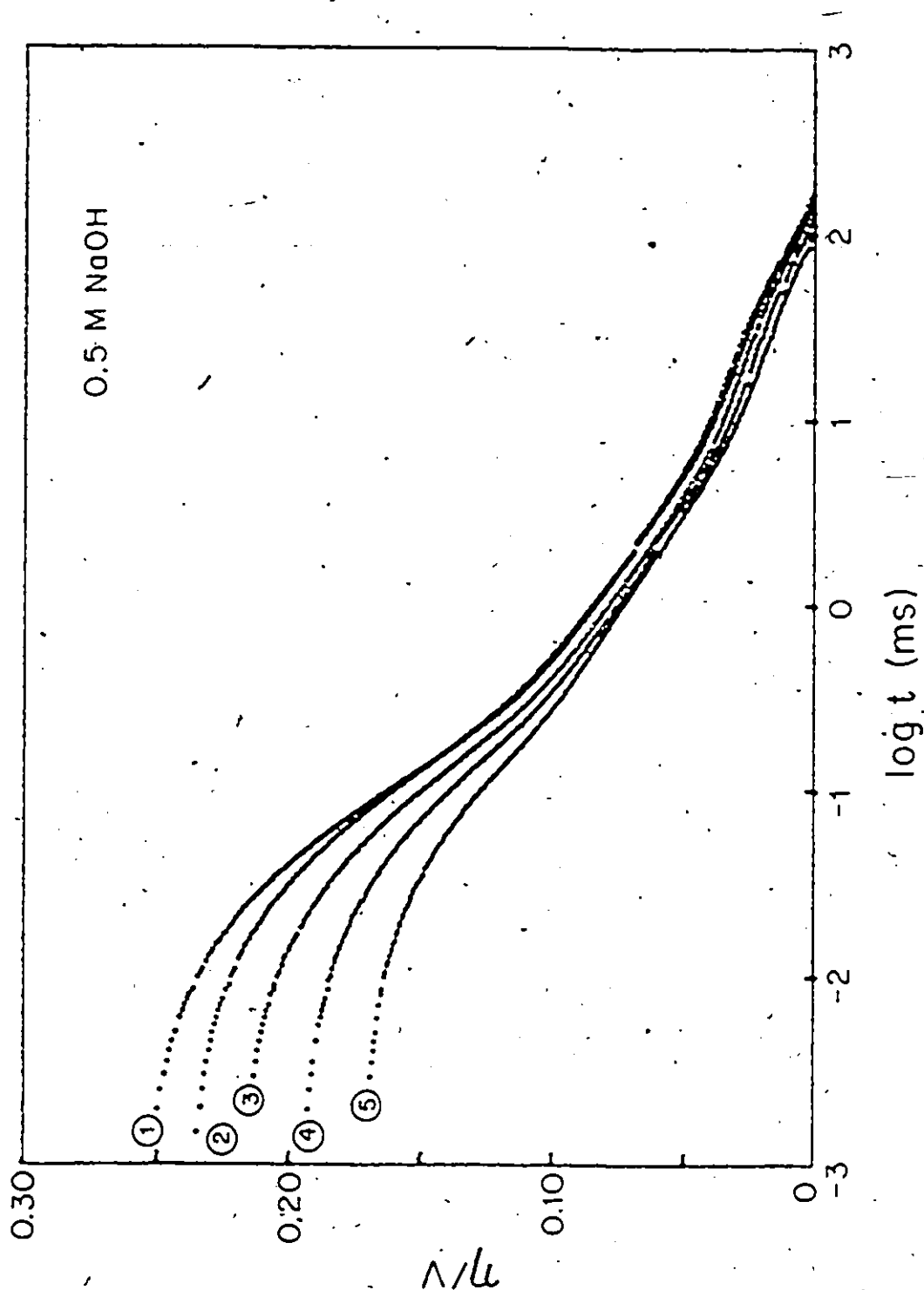


Fig. 4.38 Potential-decay plots for the h.e.r. at anodically activated Pt at a rotation rate of 3600 r.p.m. in 0.5 M NaOH at 296K for interruption of polarization at 5 current densities: 1) 0.044; 2) 0.037; 3) 0.029; 4) 0.024 and 5) 0.018 A cm⁻².

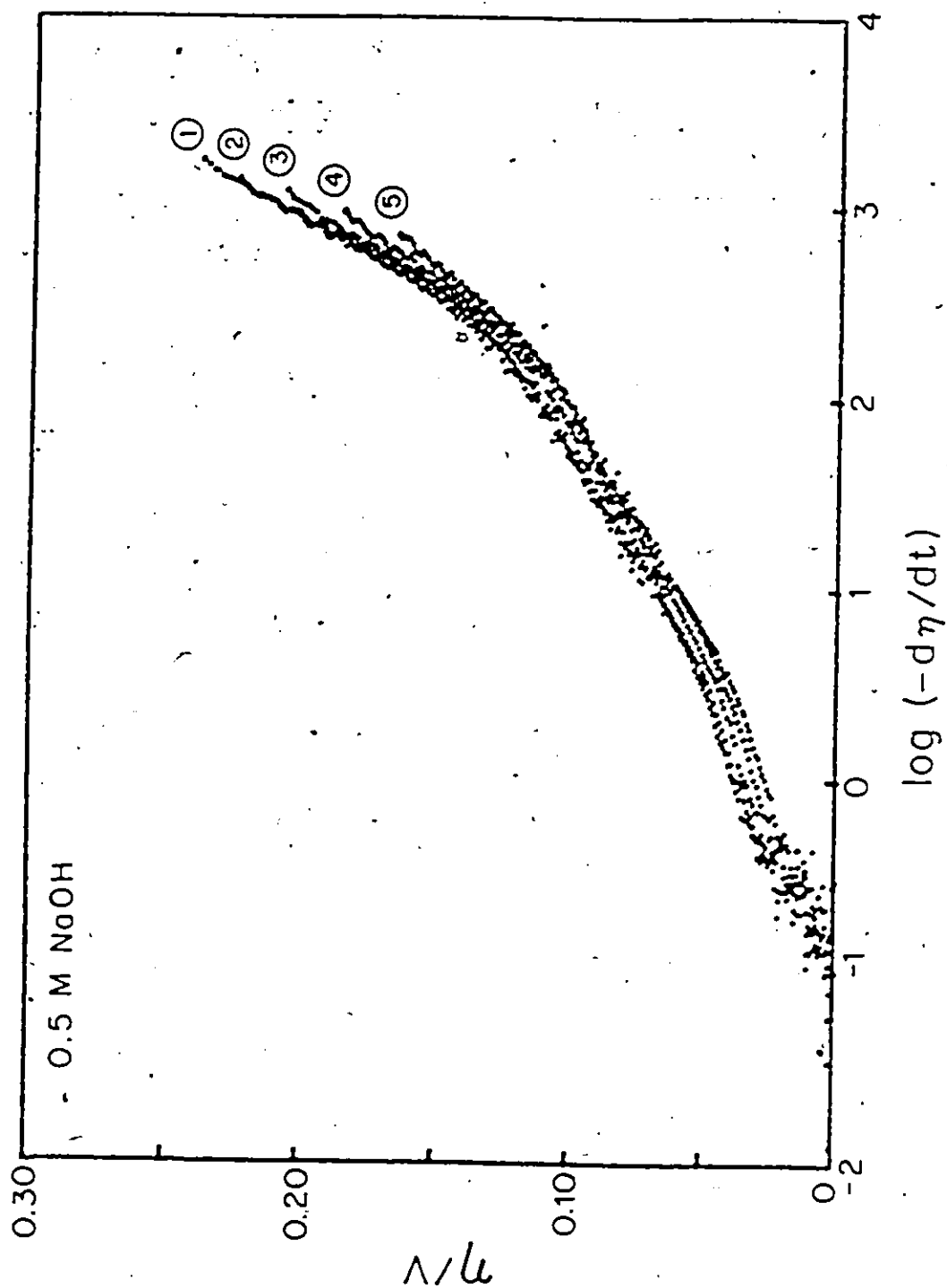


Fig. 4.39 Plots of η vs $\log(-d\eta/dt)$ for the same data as shown in Fig. 4.38.

The potential decay behaviour for the h.e.r. at Pt electrodes is more complex than at Ni and Ni-Mo-Cd plated alloy electrodes because the Tafel slope, b , is a function of η at high η (the Tafel "lines" are curved).

4.3.1.3 Pseudocapacitance Behaviour of Adsorbed o.p.d. H

(a) Acidic solutions

The evaluation of the pseudocapacitance behaviour of adsorbed o.p.d. H species can be made directly with eqn. (3.13), using the η vs $\log i$ data (Fig. 4.34) together with the $\eta(t)$ behaviour differentiated to give dn/dt (in Fig. 4.37). Fig. 4.40(a) shows C_ϕ , thus derived, for the Pt electrode in 0.5 M H_2SO_4 solution as $f(\eta)$. The four curves in Fig. 4.40(a) correspond to the curves in Figs. 4.34 and 4.37, i.e. curve 1 is for the anodically activated electrode while curves 2, 3 and 4 are for the aged electrodes after cathodic polarizations at $\eta = ca. 0.050$ V for 15, 30 and 60 min., respectively. Evidently, there is a continuous variation of C_ϕ with η , exhibiting a maximum as in fact is expected theoretically³⁷⁻⁴⁰. However, it is seen that the half-width is narrower than that required for Langmuir adsorption (cf. ref. 38) and corresponds to $g = -2$ in eqns. (1.14) and (1.16) i.e. some attractive interactions are involved. When $\eta > 0.060$ V, C_ϕ decreases rapidly and reaches the value of C_{dl} ($25 \mu F cm^{-2}$) finally. This can be seen more clearly in the extended profile shown in Fig. 4.40(b)

The corresponding H deposition charges are evaluated by integrating $C_\phi(\eta)$ with respect to η [peak areas in Fig. 4.40(a)].

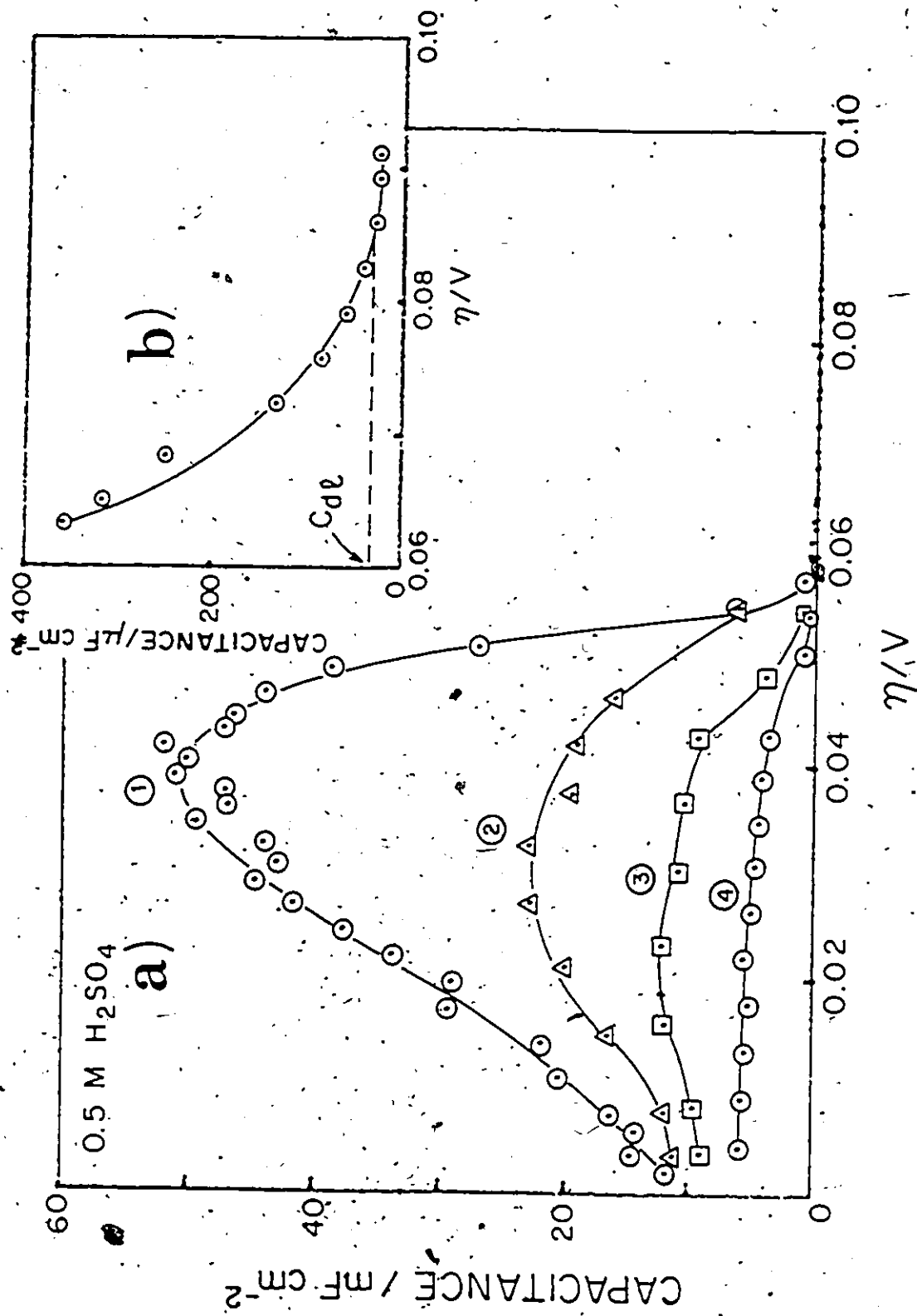


Fig. 4.40 (a) Capacitance C vs overpotential η for the h.e.r. at Pt for the same conditions as in Figs. 4.34 and 4.36. (b) Inset figure: extended profile at high η of curve 1 in Fig. 4.40a to show clearly the double-layer capacitance, C_{dl} , as $f(\eta)$, approached limitingly above 0.085 V overpotential.

By assuming the H deposition charge for a monolayer is the same as that for a Pt(111) surface, i.e. $q_1 = 210 \mu\text{C cm}^{-2}$, the apparent coverage of Pt in equivalent monolayers of H could be evaluated, as shown in Table 4.4.

Table 4.4 Numbers of equivalent monolayers of o.p.d. H at a Pt electrode in acid for activated and variously aged electrodes, calculated from the data in Fig. 4.40(a)

Cathodic polarization time (min.)	Type of electrode treatment	Surface charge ($\mu\text{C cm}^{-2}$)	No. of equivalent monolayers
0	activated	1866	8.8
15	aged	915	4.3
30	aged	519	2.4
60	aged	247	1.1

It is seen from Table 4.4 that the apparent coverage by adsorbed o.p.d. H species at an activated Pt electrode is 8.8 equivalent monolayers, which is a surprising result. We shall discuss the significance of this in Section 4.3.1.4.

It is noted that as the Pt electrode becomes more and more "poisoned" (at longer cathodic polarization times), the apparent surface coverage by o.p.d. H (and also the u.p.d. H - see Section 4.3.1.6) decreases and finally only ca. one equivalent monolayer of o.p.d. H is observed. This can be related to the linear Tafel plot, with $b = 0.125$ V, observed at high η (see curve 4 in Fig. 4.34).

(b) Alkaline solutions

Fig. 4.41(a) shows C as $f(\eta)$ for an activated Pt electrode in 0.5 M NaOH solution, corresponding to the polarization and decay data in Figs. 4.35 and 4.39, while Fig. 4.41(b) shows C_{dl} vs η based on the same data plotted on an extended scale; a reasonable value of $C_{dl}^{-1} = 25 \mu F cm^{-2}$ is found under these conditions. Integrating the $C(\eta)$ vs η profiles in Fig. 4.41(a) gives an H deposition charge of $80 \mu C cm^{-2}$ which corresponds to $\theta_H = 0.38$, assuming again $q_1 = 210 \mu C cm^{-2}$

Equation (3.13) indicates that, when $C_\phi \rightarrow 0$, the ratio $i(\eta)/(-d\eta/dt)$ will be constant if the value of C_{dl} is relatively constant. This is best illustrated by the behaviour of the h.e.r. at Au in both acid and alkaline solutions shown in Fig. 4.33. It is seen from Fig. 4.42(a) that the curve 1 for η vs $\log i$ and the curve 2 for η vs $\log(-d\eta/dt)$ are almost parallel straight lines each having a slope of 0.125 V, except over the low η region of curve 2 where there is a slight deviation from the straight line, which indicates a small C_ϕ in the low η region, as shown in Fig. 4.42(b). A total o.p.d. H deposition charge, $22 \mu C cm^{-2}$, and fractional coverage, $\theta_H = 0.1$, can be calculated from Fig. 4.42(b).

The adsorption behaviour can be related to the forms of the Tafel plots (Fig. 4.40(a) with 1; Fig. 4.41(a) with 2) in the acid and alkaline solutions. It can be seen that the potentials at which H adsorption approaches a limiting value, or saturation,

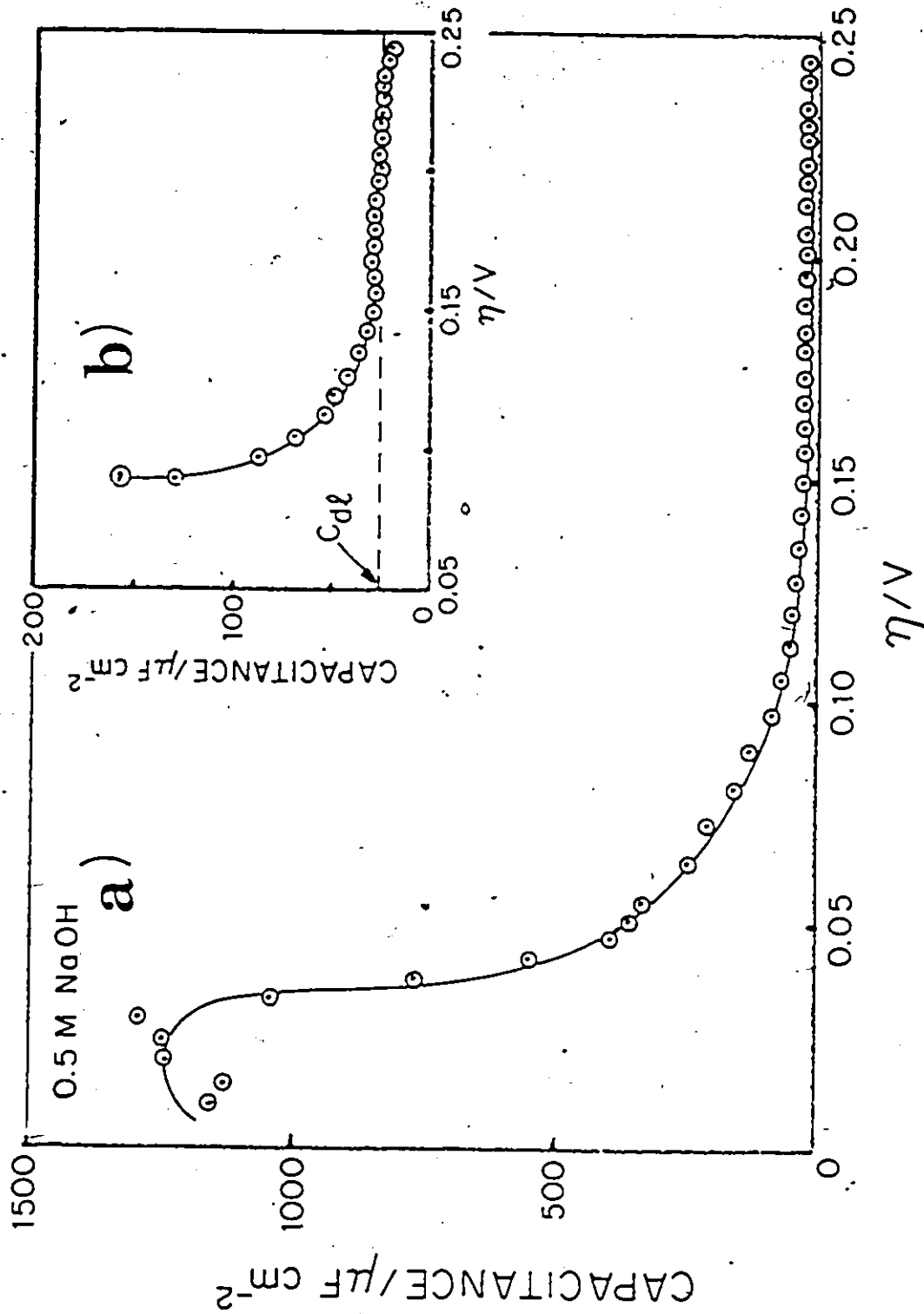


Fig. 4.41 (a) Capacitance C vs overpotential η for the h.e.r. at anodically activated Pt for the same conditions as for curve 1 in Figs. 4.35 and 4.38. (b) Inset figure: extended profile of the curve in Fig. 4.41a to high η to show clearly the double-layer capacitance, C_{dl} as $f(\eta)$, approached limitingly above 0.15 V overpotential.

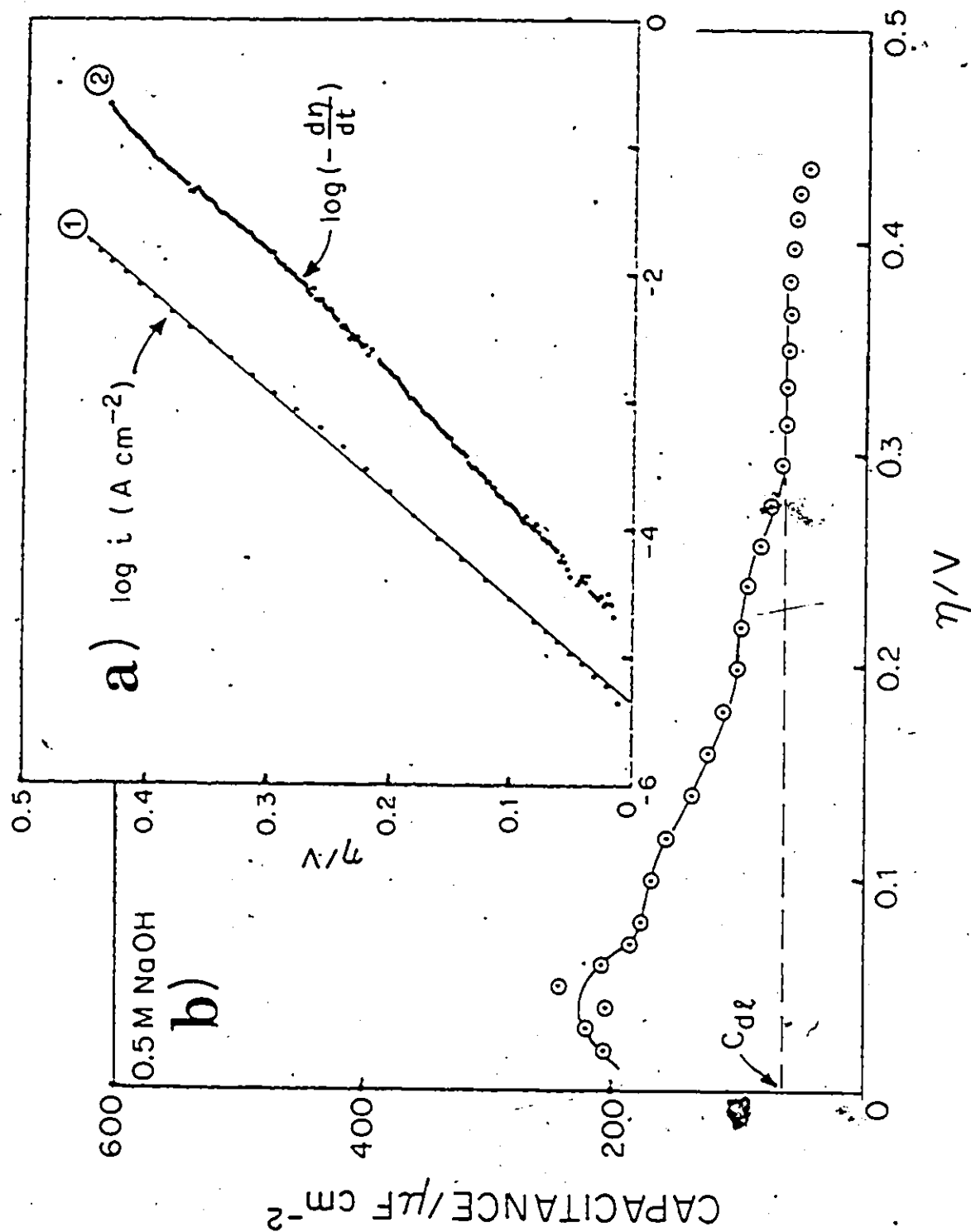


Fig. 4.42 (a) Inset figure: 1) Tafel plot and 2) plot of η vs $\log(-\frac{d\eta}{dt})$ for the h.e.r. at aged Pt for the same conditions as in this main figure. (b) Capacitance C vs overpotential η for the h.e.r. at an aged Pt electrode in 0.5 M NaOH for the same conditions as for curve 2 in Fig. 4.35.

(0.060 V in acidic and 0.100 V in alkaline solution) are, as theoretically expected (see Section 4.3.1.5), the potentials at which Tafel relation starts to become curved (for the H recombination mechanism).

4.3.1.4 The Role of o.p.d. H in the Electrocatalytic Behaviour of Pt and the Formation of a Pt-hydride Phase

The H adsorption behaviour at Pt in acid solution, where the apparent coverage is ca. 8 equivalent monolayers of H, is radically different from that in alkaline solution where θ_H is always found to be < 1 . This is strikingly illustrated by comparing the actual potential decay and the $\log -d\eta/dt$ plots in Figs. 4.36,37 with those in Figs. 4.38,39. This difference is maintained with activated electrodes that in both acid and alkaline solutions support a full monolayer of u.p.d. H and the behaviour observed is not changed by pre-electrolysis of the already very pure solution in pyrodistilled water. Therefore the effect appears to be real, unconnected with any adventitious poisoning in the alkaline solution experiments. Also, fresh active electrodes, both in acid and alkaline solution, each give u.p.d. H monolayer charges that are the same within 5%.

Since it is difficult to cover an electrode with a film of H 8 actual monolayers in thickness, one possibility of explaining the behaviour is that the o.p.d. H at Pt in acid solution is in the form of an hydride in the near-surface region of the Pt interface. This suggests that the specially favorable electrocatalytic activity of Pt in acid solution for the h.e.r. and for

hydrogenation arises because of the presence of this electroactive surface hydride phase on which, or by means of which, proceed the elementary steps of the h.e.r. We have to recognize, however, that the derivation of C_ϕ through eqn. (3.13) implies the assumption, for Pt, that the Faradaic reaction resistance for discharge of H (cf. the equivalent circuit shown in Fig. 3.4) is substantially smaller at all potentials than that corresponding to the rate-constant(s) for either of the H desorption steps; that is, that a desorption step is uniquely rate-controlling as has usually been indicated for the h.e.r. at Pt. Nevertheless, even if the above condition regarding the Faradaic resistances does not obtain, it is unclear how that situation could then lead, as an artifact, to the high C_ϕ and corresponding large θ_H values that are obtained for Pt in acid solutions. We should mention here that a.c. impedance measurements will be shown in the next section for Pt electrodes under identical conditions to those employed in the potential decay work and also lead to large pseudocapacitance values for o.p.d. H in acid solutions; with a maximum, and actual values at various overpotentials that are in quite good agreement with the potential decay results. Therefore the high values and resulting large apparent "coverages" are not artifacts of the potential decay method. This is also shown by an analysis recently carried out by Harrington in this Laboratory of the full kinetic theory of potential decay without reference to any arbitrary equivalent-circuit representation.

It is interesting that no indication exists from u.p.d. H work at Pt in acid solution that any more than a single monolayer

of H is deposited up to a potential of ca. $+0.050$ vs $E(H_2)$, even with holding the potential constant at that value for some time. Evidently potentials more negative than the reversible H_2/H^+ value are required for generation of this state of sorbed H at Pt in acid solution.

Since the behaviour does not arise at Pt in alkaline solution where the discharged H arises from the H_2O molecule rather than " H_3O^+ ", it seems that if it is surface hydride formation that is occurring, at Pt in acid solutions, it may require direct injection of a proton from H_3O^+ rather than discharge of an H atom in a neutral state. Some support for this arises from work of Palczewska¹⁹¹ who found that sorption of hydrogen into Fe films from the gas phase only took place when H_2 was dissociated and ionized to H^+ rather than being just dissociated to neutral H atoms. The results shown in section 4.1 also give indications that the high activity of Ni-Mo-Cd plated electrodes for the h.e.r. is associated with the formation and presence of a Ni-Mo-hydride phase.

Since the "multilayer" sorption of H at Pt in acid solution is an unusual, and perhaps unexpected but important result, its reproducibility was checked in several separate experiments and by another researcher in this laboratory. However, the very different delay regions seen in the $\eta(t)$ behaviour in Figs. 4.36 and 4.38 for acid and alkaline solutions, that correspond to different "CR" behaviour, are directly apparent from these figures.

The present results show that in the following sequence of states of the electrode investigated: unactivated Pt in alkaline

solution; activated Pt in alkaline solution; unactivated Pt in acid; and activated Pt in acid solution, the adsorption of o.p.d. H increases while the h.e.r. rate is also increased at a given overpotential. Thus, improvement of the electrocatalytic activity of the Pt electrode is directly associated with an increase of coverage or sorption by o.p.d. H. Also, as shown below, the u.p.d. coverage derived from CV is directly related to the extra o.p.d. coverage evaluated from the potential decay results.

With regard to the apparent generation of an hydrided state of the boundary region of the Pt electrode in acid, it is reasonable to suppose that such a surface would have weaker affinity for chemisorbed H, which could lead to an enhanced rate of H atom recombination desorption (see section 1.6). It may be presumed that entry of H into the surface region of Pt would promote d-band filling in that region, as with bulk alloys of H or Au with Pd (cf. the work on catalysis and adsorption in relation to d-band filling¹⁷⁶⁻¹⁷⁸). The effect of weakening the adsorption bond of H to Pt can, of course, go in either direction, depending to which side of the "volcano relation" (see Fig. 1.6) the experimental conditions of H coverage and bond strength correspond. However, since at Pt, we are probably on the right-hand side of the volcano relation (high coverage and large bond strength of the electroactive o.p.d. H species) any factor, such as hydriding, that could weaken the bond of these H species at the Pt metal interface, would tend to increase the rate of recombination, (see section 1.6).

We have also considered the possibility of dissociative readsorption of H from H₂ (cf. ref. 111 for Ni) at active Pt

electrodes during decay but that process seems unlikely since the net reaction must always be in the direction of H_2 formation at the cathodic potentials in our experiments. In the method of refs. 110 and 111, readsorption with extra charge for oxidation of the resulting H, is possible* since anodic transients are taken to potentials positive to the H_2 reversible potential.

Although our apparent "fractional" coverages are > 1 , they reach a sharp limit with increasing current-density while the supposed readsorption effect (at Ni, 111) was found to increase continuously to large extents with increasing current-density. Note that at Ni, under otherwise similar conditions to those ref. 111, the decay method does not give anomalously high coverages and, in fact, limiting coverages by o.p.d. H of only 25 to 30% are found (see section 4.1) which can be rationalized kinetically.

4.3.1.5 Mechanisms

(a) Acidic Solution

i) Activated electrodes

The reaction schemes for the h.e.r. were shown as eqns. (1.6), (1.7) and (1.8) in section 1.4. Since the present experiments show that the apparent o.p.d. H coverage is large on a Pt electrode in acid, the initial discharge step may be expected to be in quasi-equilibrium. In the absence of more definite information, the electrochemical adsorption behaviour of the kinetically-involved

*This is what gave rise to θ_H values $>$ and $\gg 1$ in that work¹¹¹ in the case of Ni.

o.p.d. H at the interface of the supposedly hydrided surface region with the solution will be expressed by the familiar adsorption isotherm (eqn. 1.11). The corresponding pseudocapacitance is shown in eqn. 1.13.

Given the result that the coverage by o.p.d. H is apparently substantial and if step (1.8) is rate-controlling, a limiting current would be expected at high η ; on the other hand, if step (1.7) is rate-controlling there should be a linear Tafel relation having a slope near 0.118 V at 298 K. However, these expectations are not fulfilled experimentally and, in fact, the experimentally observed variation of H coverage with η at Pt does not evidently correspond to a Tafel relation determined uniquely by H recombination kinetics¹⁸⁵⁻¹⁸⁷.

The Tafel relation observed for the h.e.r. at activated Pt electrodes in acid, as shown in Fig. 4.34 (curve 1), suggests that the recombination and the electrochemical-desorption steps are involved in parallel paths but the recombination step makes the greater contribution to the reaction rate at low η , while the electrochemical-desorption step becomes dominant at high η . Thus, the total current-density should be expressed in the form:

$$i/2F = k_2(c_{H^+})\theta_H \exp(B\eta F/RT) + k_3\theta_H^2 \quad (4.23)$$

or in forms involving the g factor, eqns. (1.14, 1.16). In the r.h.s. of eqn. (4.23), the first term is written for the rate of the electrochemical-desorption and the second for the recombination pathway. It is noted that the faster reaction characterizes the

kinetics in the case of parallel reactions.

It is interesting to see if the observed Tafel plots can be simulated using eqn. (1.11) with eqn. (4.23) for the parallel pathway, as shown in Fig. 4.43. The following arbitrary values of the required constants are used: $K_1 = 0.1$, $k_2 = 0.1$, $k_3 = 13$, $c_{H^+} = 1$, $T = 298$ K. Curve 1 in Fig. 4.43 represents the contribution from step (1.7) alone ($k_3 = 0$) while curve 2 is that for step (1.8) alone ($k_2 = 0$); curve 3 represents the Tafel plot for both contributions in a parallel pathway. It is seen that the form of the Tafel plot thus calculated (curve 3 in Fig. 4.34) is very similar to the form of the experimental Tafel plot (curve 1 in Fig. 4.34). Notice that the linear region at low η with a slope of 0.036 V can be accounted for with θ_H represented as $f(\eta)$ according to eqn. (1.11). Of course, while the choice of constants above is arbitrary, the important point is that the form of the observed behaviour can be closely simulated in terms of the parallel pathway. (The full kinetic analysis of the d.c. polarization behaviour using the simulated rate constants from a.c. impedance experimental data and the reaction mechanism will be discussed in the next section, 4.3.2).

ii) Aged electrodes

Since the apparent coverages by o.p.d. H on aged electrodes are also more than one monolayer (see Table 4.4), the quasi-equilibrium condition in the discharge step (eqn. 1.6) probably still holds, so that the θ_H vs η relation still follows eqn. (1.11).

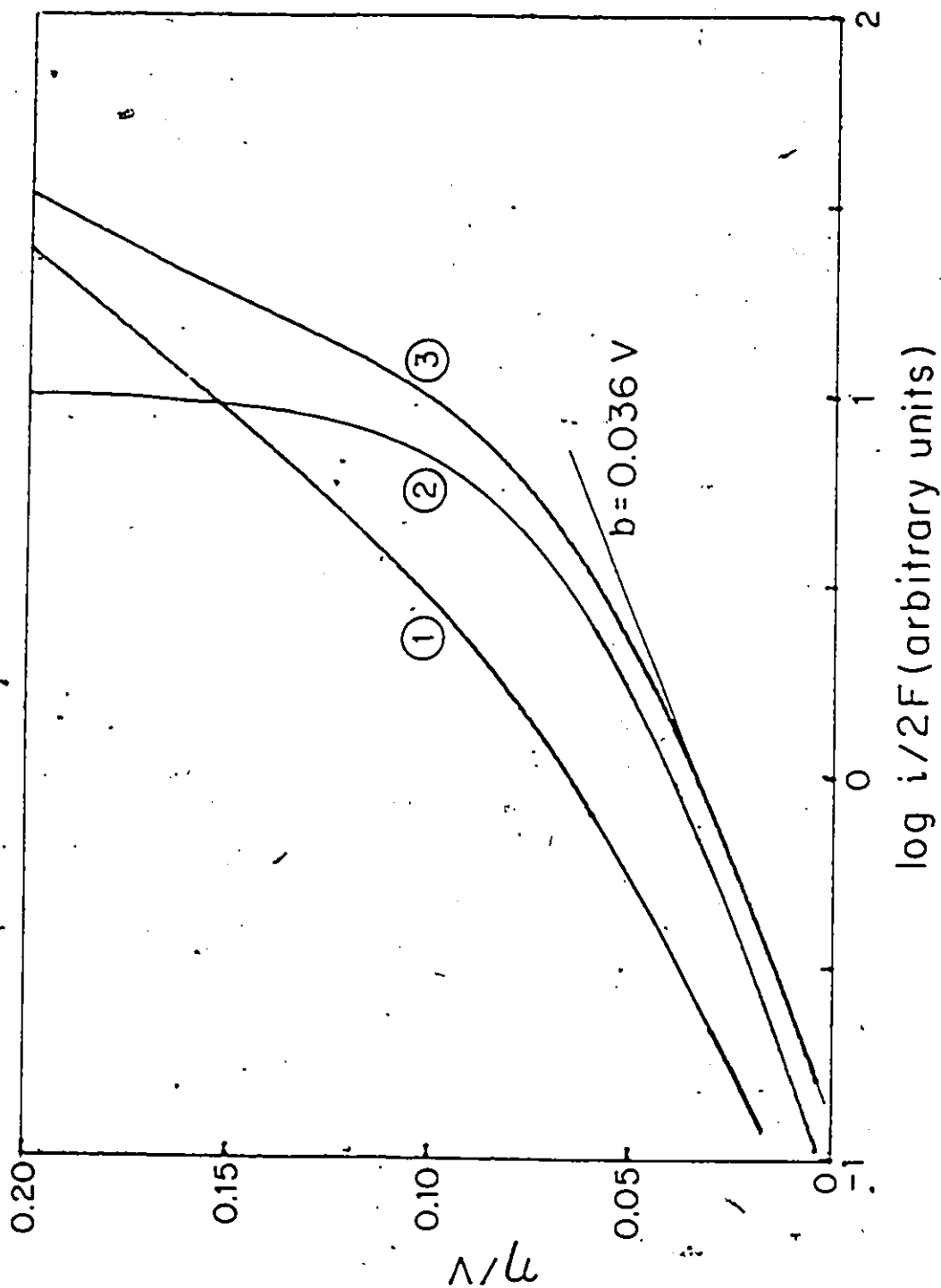


Fig. 4.43 Simulated Tafel plots for the parallel desorption pathway using eqn. (1.11) with eqn. (4.23) taking $K = 0.1$, $C_H^+ = 1$, $T = 298K$; 1) $k_3 = 0$, $k_2 = 0.5$; 2) $k_2 = 0$, $k_3 = 10$ and 3) $k_2 = 0.5$, $k_3 = 10$ (arbitrary units).

Fig. 4.40(a) shows that the C_ϕ vs η curves for different aged electrodes have similar shapes. This suggests that they should correspond to similar θ_H vs η relations if it is assumed that q_1 is different for each curve (see Table 4.4). We note that the peak potentials shift to lower η values as time of polarization increases (see Fig. 4.40 a), which indicates that the rate constant ratio k_1/k_{-1} , for that amount of o.p.d. H that can be accommodated on and in the surface, increases with increasing time, though the total apparent coverages decrease with time of polarization due to the poisoning effect.

Simulated Tafel plots for aged electrodes were also calculated using eqns. (1.11) and (4.23) for the parallel mechanism, as shown in Fig. 4.44, where the parameters chosen are indicated in the caption. Evidently the experimentally determined Tafel plots taken at aged electrodes (Fig. 4.34) can be quite well simulated by the calculated ones, based on the parallel pathway, as shown in Fig. 4.44. In order to account for the observed progression of Tafel relations with time of polarization, corresponding to deactivation of the electrode (diminution of o.p.d. H coverage from 8.8 to 1.1 equivalent monolayers) an exponentially decreasing rate-constant ratio, k_3/k_2 , with time is required to account for the time-dependent behaviour.

In summary, at aged Pt electrodes in acid, the parallel mechanism can also apply; the rate of the recombination step contribution decreases exponentially with cathodic polarization time.

(b) Alkaline solution

1) Activated electrodes

The paths of the h.e.r. in alkaline solution are similar to those in acid solution except that H is discharged from H_2O rather than from H_3O^+ , (see eqns. 1.6b, 1.7b). We denote this by priming the rate constant symbols k_1 , k_{-1} and k_2 . In alkaline solution, discharge is usually more difficult than in acid, so $k_1' < k_1$ and $k_2' < k_2$. If k_3 remains independent of pH (apart from anion adsorption effects), the recombination pathway component will tend to be favoured.

The fact that the o.p.d. H coverage, $\theta_{lim,H}$ is now less than 1 but still appreciable [$\theta_{lim,H} = 0.38$ for an activated electrode, see Fig. 4.41(a)] indicates that the rate constant of the initial discharge step is comparable to that of the electrochemical-desorption step, i.e. quasi-equilibrium in the former is not maintained. This kind of kinetic situation has to be treated by the steady-state method as in the previous discussion of o.p.d. H coverage at Ni and Ni-Mo-Cd plated electrodes (section 4.1.1.4).

The relevant rate equations for processes 1, 2 and 3 (eqns. 1.6, 1.7 and 1.8, respectively) are shown in eqn. (3.37). The eqns. for steady-state θ_H can be solved by setting eqn. (3.18) equal to zero ($r_1=0$), giving $\theta_H(\eta)$ (eqn. 3.39) and $C_\phi(\eta)$ (eqn. 3.40) relations (see section 3.2.2.3).

Fig. 4.45 shows C_ϕ vs η and θ vs η plots calculated from eqns. (3.40) and (3.39), respectively. The parameters taken are shown in the caption of Fig. 4.45. The simulated Tafel plots,

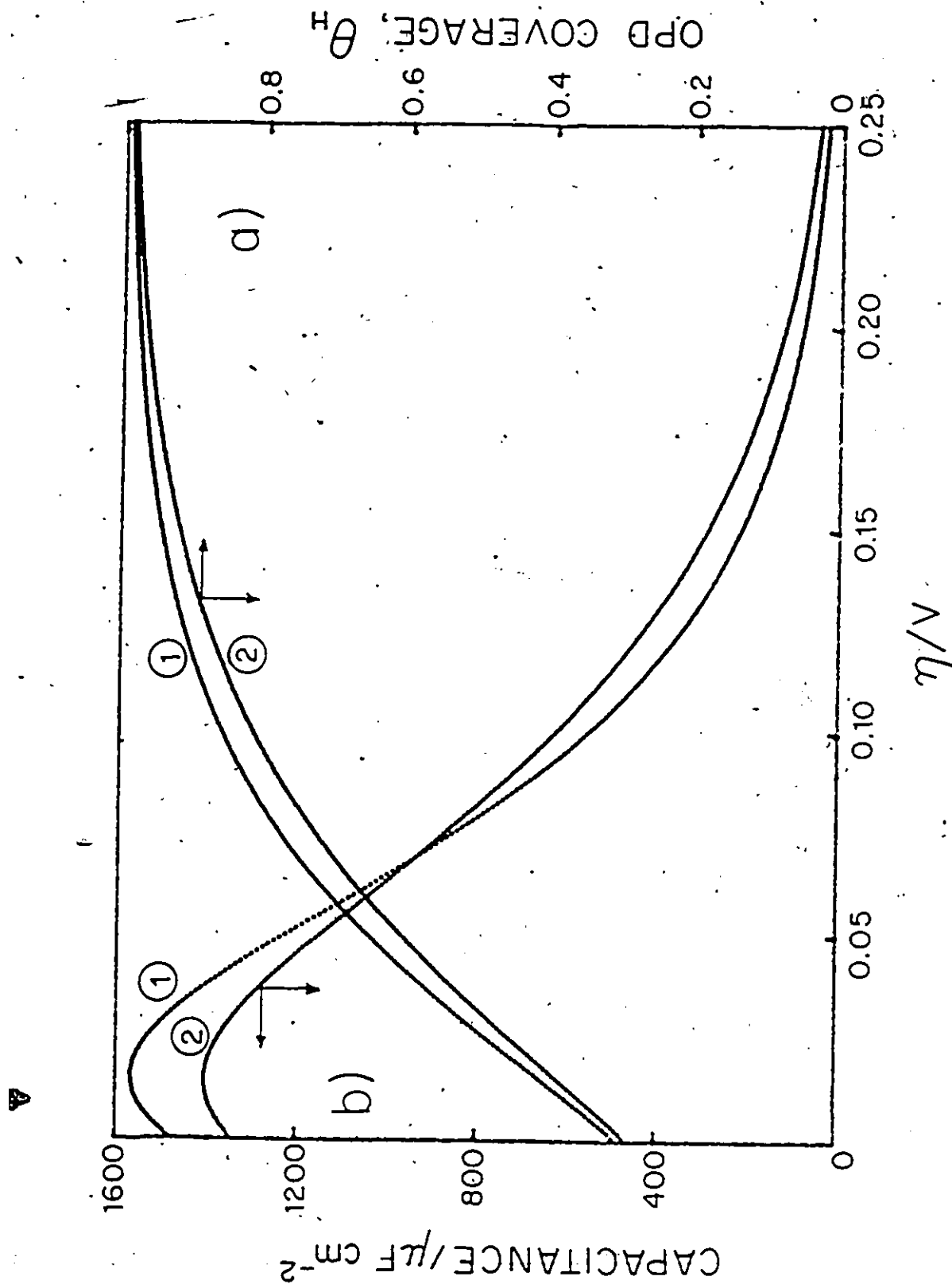


Fig. 4.45 Calculated plots of a) θ_H vs η for 2 k_3/k_2 values, using eqn. (3.39); b) c vs η using eqn. (3.4), taking $C_{OH^-} = 1$, $q_1 = 210 \mu\text{e cm}^{-2}$, $T = 298\text{K}$, $k_1 = 50$, $k_{-1} = 100$, $k_2 = 0.1$ with 1) $k_3 = 50$ and 2) $k_3 = 80$ (arbitrary units).

which correspond to the $C_\phi(\eta)$ and $\theta_H(\eta)$ relations, are shown in Fig. 4.46, and were calculated for the parallel mechanism using eqn. 4.23, taking the same parameters as for Fig. 4.45.

Comparing the behaviour shown in Fig. 4.46 with that in Fig. 4.35 and in Fig. 4.45 with Fig. 4.41(a), it is seen that the parallel mechanism also applies in alkaline solution for the activated electrode; moreover, the observed behaviour is accounted for if, for the initial discharge step, a rate constant is taken comparable to those of the second parallel steps ($k_1/(k_2+k_3)=50/80$) while the recombination step has the greater contribution to the total rate of the parallel desorption steps ($k_3/k_2=80/0.1$ is required).

(ii) Unactivated electrodes

Since it is shown here that, for alkaline solutions at unactivated Pt electrodes, the coverage of o.p.d. H is relatively low [$\theta_H = 0.1$, see Fig. 4.42(b)], the rate-constant for the initial discharge step must now be relatively small, leading to a linear Tafel relation with a slope of 0.120 V (see Fig. 4.35, curve 2).

4.3.1.6 Relation between u.p.d. and o.p.d. H Coverage

The measurement of the u.p.d. H in the present experiments, which was described in section 2.3.4, was made in a slightly different way from that in previous work in this laboratory¹⁵⁰. The progressive decrease of the u.p.d. hydrogen charge from that measured without prior cathodic polarization for time t

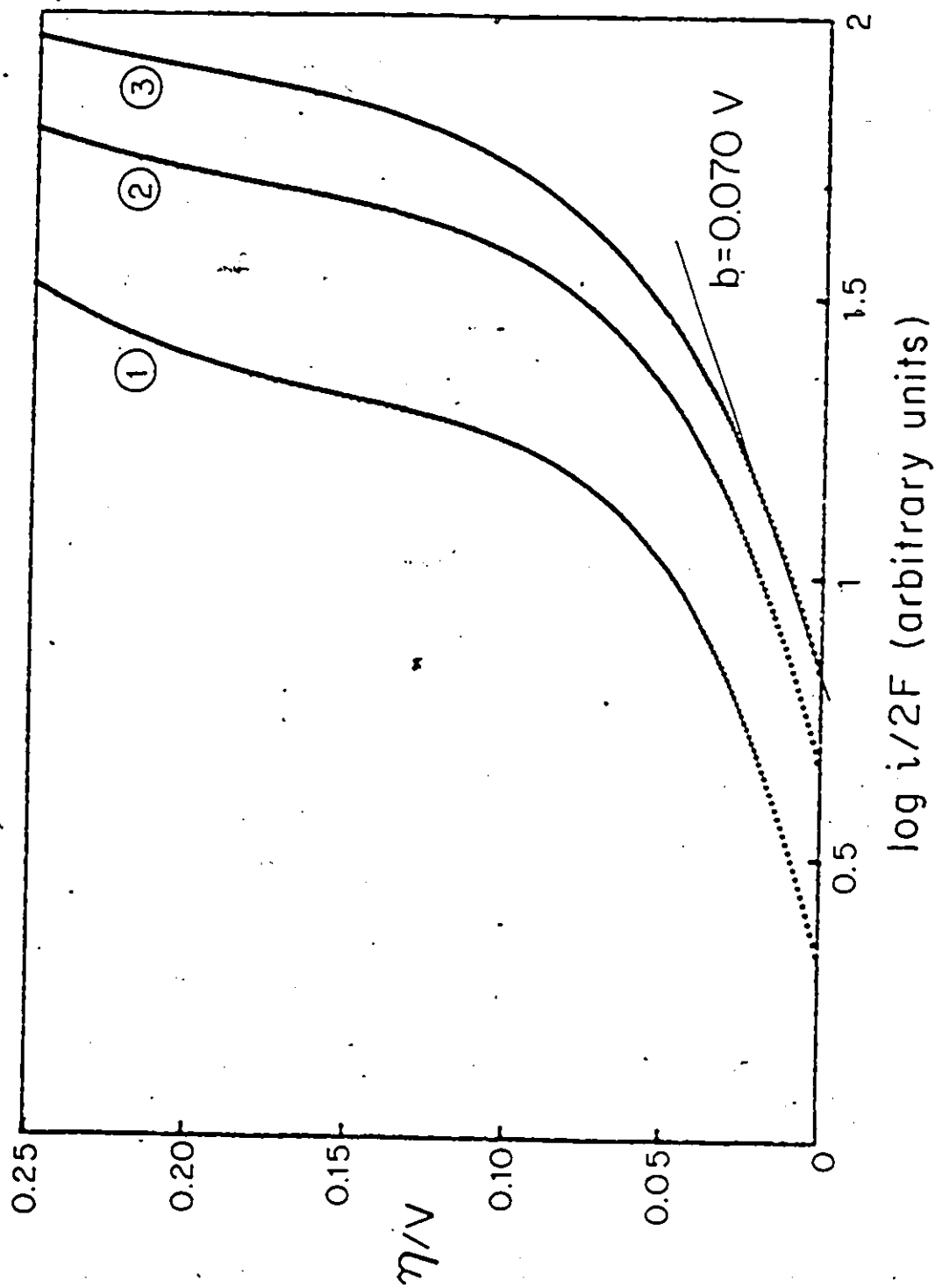


Fig. 4.46 Simulated Tafel plots for the parallel desorption pathway using eqn. (3.39) with eqn. (4.23) taking: $C_{OH^-} = 1$, $T = 298K$, $k_1 = 50$, $k_{-1} = 100$, $k_2 = 0.1$ with 1) $k_3 = 20$, 2) $k_3 = 50$ and 3) $k_3 = 80$ (arbitrary units).

indicated that the surface was becoming blocked by adsorption or deposition of impurities during the time t of cathodic polarization.

The inset (b) of Fig. 4.47 shows the resulting cyclic-voltammetry profiles for Pt in 0.5 M H_2SO_4 . Curve 1 is the normal profile for high-purity conditions, i.e. without cathodic polarization or impurity accumulation, while curves 2, 3, 4, 5 and 6 are the profiles recorded after cathodic polarization at $\eta = 0.050V$ for 5, 10, 20, 30 and 60 min., respectively. It is seen that the u.p.d. H is successively reduced as the cathodic polarization time is increased, due presumably to the progressive accumulation of deposited and/or adsorbed impurities^{82,150}, as found in earlier work quoted here.

The relative changes of coverages both by u.p.d. and o.p.d. H with cathodic polarization time can be calculated if the "full coverage" charge is taken as $210 \mu C cm^{-2}$ for the u.p.d. H and $1880 \mu C cm^{-2}$ (8.8 equivalent layers) for the sorbed o.p.d. H.

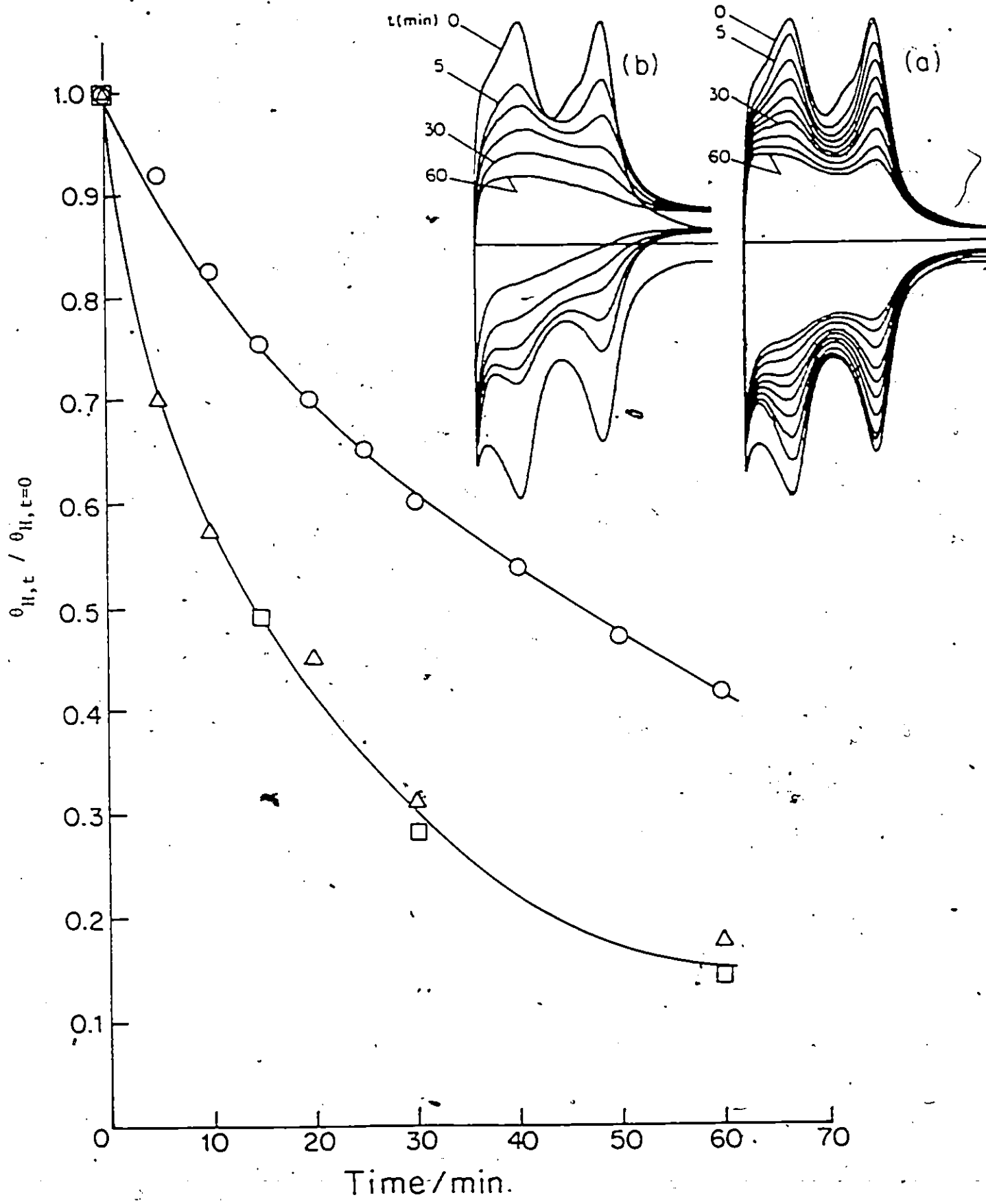
The results are shown in Fig. 4.47; (the o.p.d. data are taken from Table 4.4, the u.p.d. from the insets of Fig. 4.47). Fig. 4.47 also shows the decline of u.p.d. H coverage with time without cathodic polarization, i.e. during potential cycling between + 0.05 and +0.75 V E_{H_2} (see inset (a) of Fig. 4.47).

It is noted that the apparent relative coverages by the o.p.d. and u.p.d. H fall on the same line with time of polarization, i.e. there is a one-to-one relation between the o.p.d. and u.p.d. H, and both are related to the active adsorption sites on the electrode; however, the o.p.d. H charge is much larger (8.8x) than the u.p.d. H charge in the case of results for acidic solution.

Fig. 4.47

relative coverage, θ_H vs time of cathodic polarization for the HER at Pt in 0.5 M H_2SO_4 of $\odot$ UPD without cathodic polarization; Δ UPD after cathodic polarization at $\eta = 0.050$ V and $\square$ OPD after cathodic polarization of $\eta = 0.050$ V.

Inset figures: Cyclic-voltammetry i vs η profiles between 0.05 and 0.75 V; a) for various cycling times corresponding to the $\odot$ data in the main Fig. 4.47; b) after various cathodic polarization times corresponding to Δ data in the main Fig. 4.47.



4.3.1.7 The Effects of Impurities

Although the effects of impurities on the h.e.r. at Pt and other electrodes have been previously studied [e.g. 23,82,83,150], the mechanistic effects of "poisoning" could not previously be adequately discussed owing to lack of information on actual H coverage. From the present investigation, quantitative knowledge is provided on this matter.

Firstly, impurities tend to retard the initial discharge step in the h.e.r. at Pt electrodes; the probable mechanism is that impurities block the "active sites" for H deposition in the discharge step, so that coverage by the adsorbed o.p.d. H is decreased, leading to diminution of the discharge rate; consequently, desorption steps especially the recombination step, which depends on θ_H^2 and makes the major contribution to reaction rate in the parallel two-step pathway for active Pt electrodes, becomes retarded. As active sites become increasingly blocked by impurities, the reaction tends to become controlled by the initial discharge step.

Impurity effects not only arise by simple blocking of the electrode surface, reducing i_0 , but can also lead to a change of reaction mechanism, e.g. by retarding the recombination step, which has a low Tafel slope ($b=0.029$ V as $\theta \rightarrow 0$), and consequently diminishing its contribution to the current in the parallel reaction pathway.

Secondly, the effects of impurities are cumulative, i.e. both the coverage of u.p.d. and o.p.d. H decrease with $\ln(\text{time})$.

During a relatively short time period (1 h for acid, 0.5 h for alkaline solutions) activated Pt electrodes, even under our relatively "high purity" conditions using pyro-water, lose much of their electrocatalytic activity (90% for acid, 99% for alkaline solution).

Such effects are very important in practical applications, e.g. in water electrolyzers and fuel cells, where Pt and other electrodes are operated over long periods of time; in such cases, it seems likely that ca. 90% of electrocatalytic activity of Pt electrodes may not be effectively used!

However, the effects of impurities are removable and the present work shows (as known empirically previously) that anodic activation is a very efficient and convenient means of restoring the full capability for adsorption of o.p.d. and u.p.d. H, and thus "cleaning" the electrodes and maintaining their electrocatalytic activity in terms of high i_0 and low b values for the h.e.r.

An "anodic pulse activation" procedure could be applied in the practical case of noble metal cathodes. In our experience, the required anodic activation time is very much shorter than the cathodic polarization time. If the applied anodic potential is carefully chosen to avoid O_2 evolution, the anodic current required for activation would be very small; therefore, a very small amount of power and a very short period of time would be needed for anodic pulse activation.

4.3.2 A.C. impedance method

For clarity, the four systems studied: activated Pt in acidic and alkaline solution; non-activated Pt (with various extents of surface poisoning) in acidic and alkaline solution, will be treated separately in the four following sections.

4.3.2.1 Activated Pt in 0.5M H₂SO₄

In Fig. 4.48, Curve 1 is the steady-state polarization Tafel plot, and Curve 2 is the $\log(1/R_p)$ vs η impedance plot. The points represent the experimentally measured data obtained in 0.5M H₂SO₄ solution at the activated rotating disc Pt electrode (3600 rpm). The solid line 1 is the simulated Tafel plot using eqn. (3.41) and the solid line 2 is the simulated impedance plot of $\log(1/R_p)$ vs η , using eqn. (3.41) obtained using the following rate constant values: $k_1 = 1 \times 10^{-6}$; $k_{-1} = 1.6 \times 10^{-5}$; $k_2 = 3 \times 10^{-8}$; $k_3 = 4 \times 10^{-6} \text{ mol cm}^{-2} \text{ s}^{-1}$ and a concentration of 0.5M.

From the above, $k_3/k_2 = 133$ and it is this condition which indicates that the recombination pathway makes the major contribution to the steady-state current at low η , i.e. the recombination step is rate-determining with respect to discharge but is the predominant desorption pathway for the conditions considered here.

Evidently the large degree of participation of the recombination process in the formation of H₂ causes R_p to be $\gg R_\infty$ with the consequence that a parallel relationship arises between $\log i$ and $\log(1/R_p)$. This is in accordance with the expectation

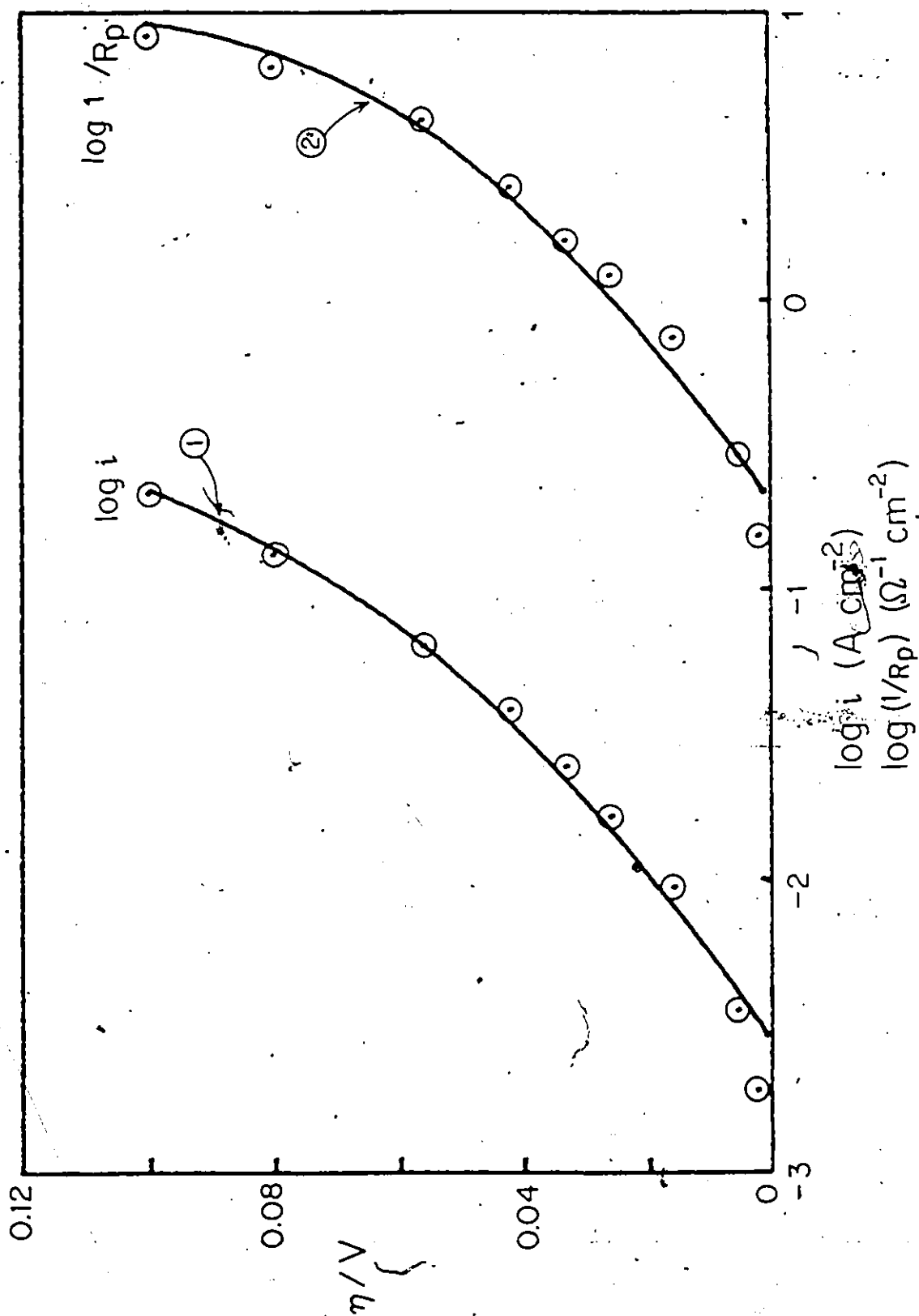


Fig. 4.48 Experimental (circled points) and simulated (solid lines) Tafel plots (1) and $\log (1/R_p)$ vs $\log i$ plots (2) for the h.e.r. at activated Pt in 0.5 M H₂SO₄.

indicated in (3.2.2.2) that R_p is associated principally with coverage relaxation effects involving a dissipative process.

Fig. 4.49 shows the complex-plane impedance diagrams for $\eta =$ a) 6; b) 18; c) 30 and d) 45 mV. The experimental data are represented by the circled points for which the underlined numbers give, in the usual way, the frequencies. The conditions are the same for Fig. 4.48. The points without circles represent the behaviour simulated by eqn. (3.29) with the same set of rate constants as for Fig. 4.48 taking $C_{dl} = 25 \mu F cm^{-2}$, $q_1 = 2300 \mu C cm^{-2}$ (see below) and $R_s = 2 \Omega cm^2$.

The impedance spectra in Fig. 4.49 exhibit two features: firstly, distorted semicircles, probably containing two components, are observed, especially in the high frequency region. These are similar to the ones observed for the h.e.r. at tungsten carbide electrodes by Armstrong and Bell¹³¹, although they did not comment on their shapes.

Comparing the experimental and theoretical impedance spectra, it can be clearly seen that a semicircle at the high frequency end corresponding to R_∞ and C_{dl} is either seriously distorted or almost absent. Since R_∞ is very small, $0.5 \Omega cm^2$ at $\eta = 6$ mV or 0.3 at $\eta = 45$ mV, with $C_{dl} = 25 \mu F cm^{-2}$, the frequency must be up to 100 kHz in order to observe such a semicircle (see Fig. 4.49) in the impedance spectrum. The maximum frequency limit of the instrument we used was 10 kHz (as in Armstrong and Bell's work too) which is evidently insufficiently high to allow reliable determination of such small R_∞ and C_{dl} values. However, Durand¹⁷⁹,

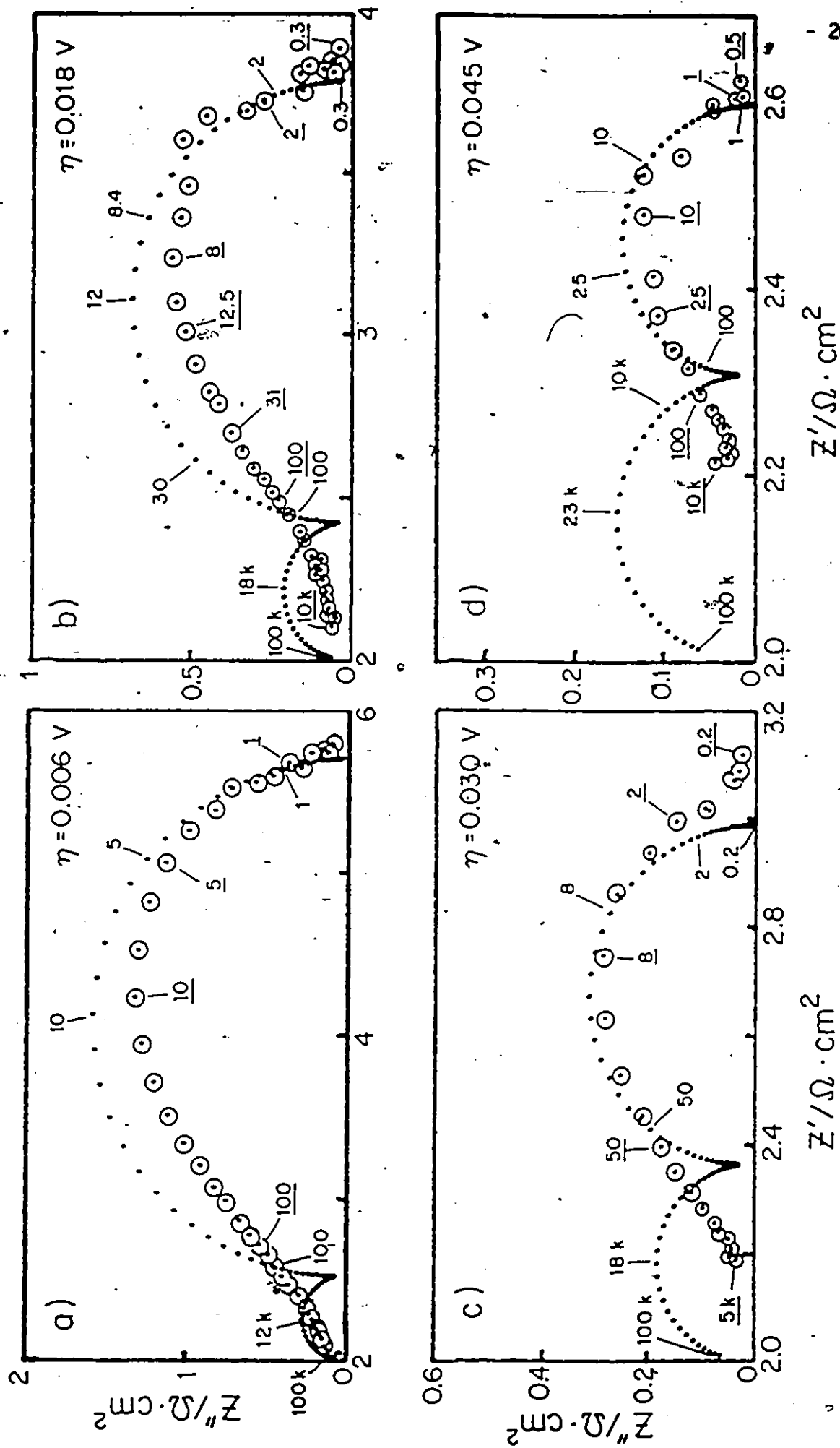


Fig. 4.49 Experimental (circled points) and simulated (points without circles) complex-plane

impedance diagrams for $\eta =$ a) 6; b) 18; c) 30 and d) 45 mV in the same condition as in Fig. 4.48. The numbers (underlined for experimental data) represent the respective frequencies (in Hz).

using frequencies up to 1 MHz, was able to observe this semicircle for the high-frequency response of the h.e.r. at Pt.

Secondly, the values of the capacitance, C_p , that can be simulated by our reaction model or approximately evaluated from the top points ($R\omega C = 1$) of the semicircles are very large, of the order of 4-40 mF cm⁻² (see Fig. 4.51). This suprizingly high capacitance is probably what leads to the unexpectedly large apparent coverage of o.p.d. H species at activated Pt in acidic solution obtained in the previous determinations by means of the potential-decay method (see section 4.3.1.3). Since the physical significance of C_p is not always explicit (section 3.2.2.2), it is necessary to seek complementary evidence for the high values ($\theta_H > 1$) of o.p.d. H coverage in terms of C_ϕ rather than C_p .

The large extent of o.p.d. H sorption follows from the unusually high value of q_1 (2300 $\mu\text{C cm}^{-2}$) that is required to simulate the frequency dispersion of the impedance observed experimentally at the lower frequencies (Fig. 4.49).

The impedance behaviour can be illustrated in another way in Fig. 4.50 which shows Bode plots of $\log |Z|$ vs $\log \omega$, with $|Z| = [(Z')^2 + (Z'')^2]^{1/2}$, $\omega = 2\pi f$ where f is the frequency in Hz. The points in Fig. 4.50 represent the experimental data which are the same as those shown in Fig. 4.49(a), while the solid lines are the numerically simulated curves for the same series of rate constants and other parameters as used for the plots given earlier in this section, taking $q_1 = 210 \mu\text{C cm}^{-2}$ for curve 2 and $q_1 = 2300 \mu\text{C cm}^{-2}$ for curve 1. In the Bode plot, the flat

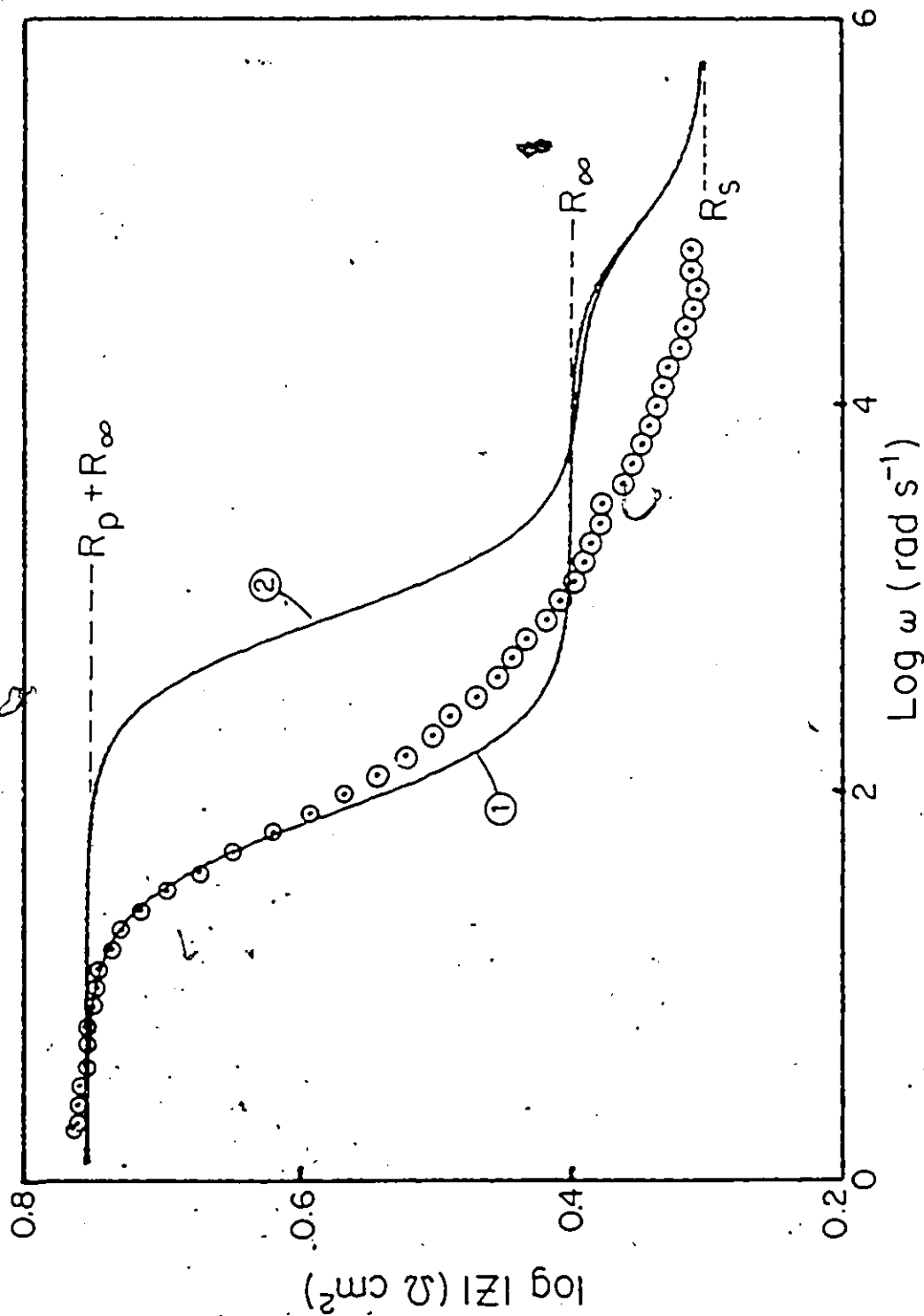


Fig. 4.50 Experimental (circled points) and simulated (solid line) Bode plots for the same experimental data and rate constants and other parameters as in Fig. 4.49(a), except, $q_1 = 2300 \mu\text{C cm}^{-2}$ for curve 1 and $q_1 = 210 \mu\text{C cm}^{-2}$ for curve 2.

region is related to the resistance and the declining region to capacitance since the impedance of capacitative components decreases as $1/\omega C$. R_s , R_∞ , R_p , C_{dl} and C_p correspond, respectively, to the regions in Bode plot that are indicated in Fig. 4.50. It can be seen from Fig. 4.50 that at the high frequency end of the curve, as with the complex-plane plots in Fig. 4.49, the experimental curve is somewhat distorted in comparison with the simulated ones. The effects of R_∞ and C_{dl} could not be observed clearly since the product $R_\infty C_{dl}$ is relatively small and, as was mentioned, the frequency range of the instrument was not high enough for this response to be detected. However, at the low frequency end, only the simulated plot (curve 1) with q_1 taken as $2300 \mu C \text{ cm}^{-2}$ fits the experimental curve closely while the simulated curve 2 for $q_1 = 210 \mu C \text{ cm}^{-2}$, which provides, of course, a very good fit to the u.p.d. H experimental data^{23,74,76}, is very far from the experimental curve (see Fig. 4.50).

The pseudocapacitance, C_ϕ , which has a clearer physical significance than C_p , and the o.p.d. H coverage, θ_H , can be calculated as a function of η from the rate constants by eqn. (3.40), as shown in Fig. 4.51. Fig. 4.51 shows interestingly that the curves of C_p , eqn. (3.43), and C_ϕ have similar shapes but the peak value of C_p is higher and θ_H is almost linearly related to η over most of the potential range investigated. The plot of the relaxation time, τ , vs η eqn. (3.42) also has a shape similar to that of the C_ϕ vs η plot; this is not surprising, since τ has similar physical significance in some cases, as discussed in (3.2.2.3) and as seen from the results for un-

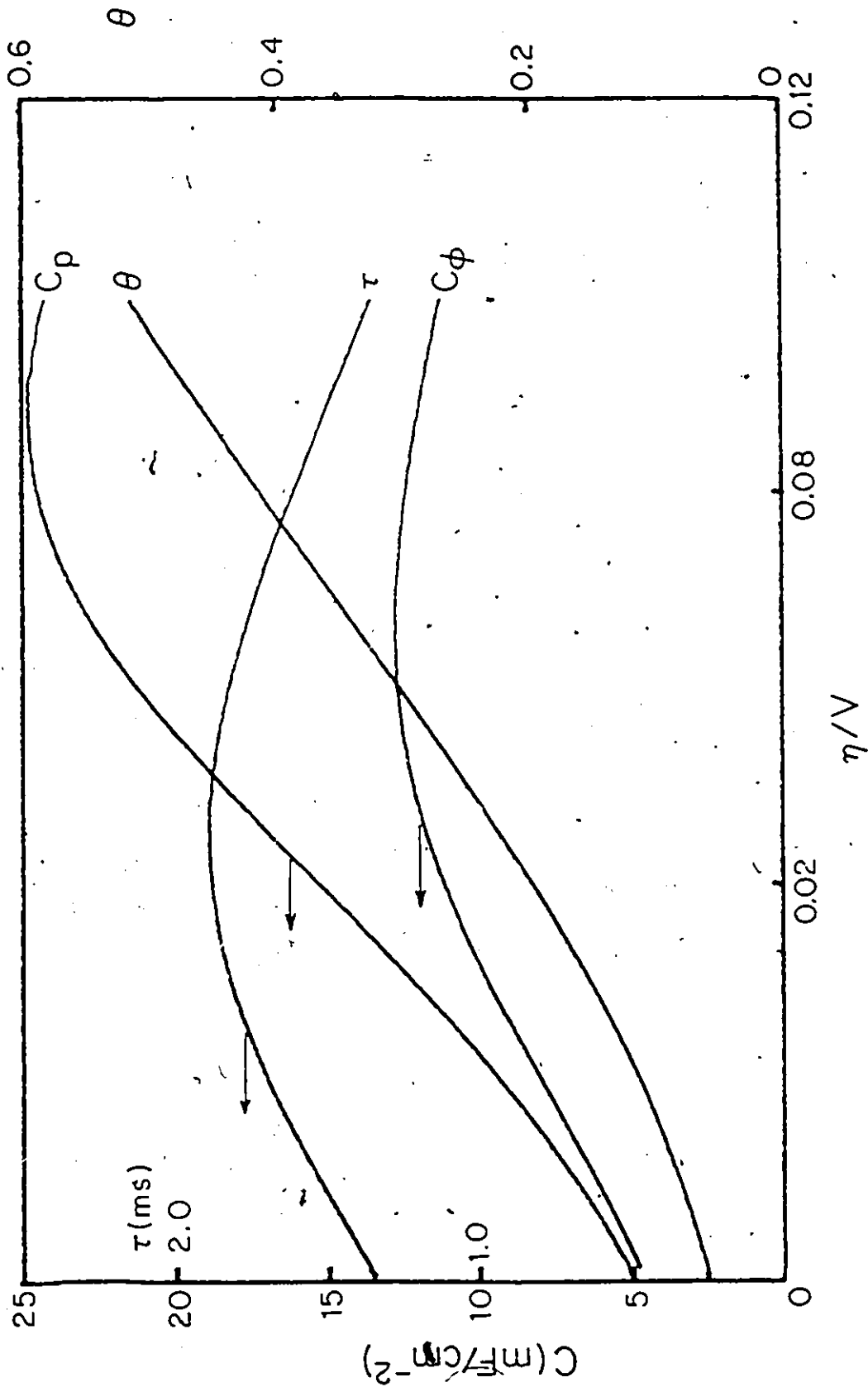


Fig. 4.51 Simulated C_p , C_ϕ , τ and θ vs η/V plots; using eqns. (3.39-3.43), with same values of the rate constants and other parameters as in Fig. 4.49.

activated Pt in acid (section 4.3.2.2).

The above result from the a.c. impedance measurements that an apparent coverage by o.p.d. H of ca. 11 "equivalent monolayers" ($2300 \mu\text{C cm}^{-2}$) (based on the u.p.d. monolayer coverage charge of $210 \mu\text{C cm}^{-2}$ for Pt(111)) arises at activated Pt, is in reasonable agreement with the figure of 8.8 layers found from previous potential-decay results (see Table 4.4). The agreement here between the results of two rather different methods for determination of o.p.d. H behaviour provides support for a) the validity of the potential-decay method and the interpretation of the decay transients that are observed and b) the reality of an unusual extent of H sorption at an active Pt electrode in acidic solution that we had tentatively attributed to surface hydride formation at Pt in the previous potential-decay work.

We suggested that the presence of a surface hydride phase weakened the metal-to-o.p.d. H bond and thus facilitated (see section 1.6) the recombination desorption step (1.8). Then the recombination step with low Tafel slope becomes the favoured desorption pathway and characterizes the kinetics at active Pt electrodes, as was concluded previously.

The recombination mechanism for activated Pt in acidic solution and the experimentally measured extents of adsorption of o.p.d. H can be confirmed as follows. If the recombination step is rate-determining and the preferred desorption pathway at Pt, the steady-state current can be calculated approximately by the relation $i = 2F k_3 \theta^2$, i.e. $i^{1/2}$ is proportional to θ . It was

found that the o.p.d. H coverage changes linearly with η (see Fig. 4.51) over most of the potential range investigated*, that is $i^{\frac{1}{2}}$ should vary linearly with η . This is illustrated in Fig. 4.52 where the results plotted are from Fig. 4.48, curve 1, i.e. the experimentally measured η vs i relation. The good linear relationship that is seen between $i^{\frac{1}{2}}$ and η provides additional support for the consistency of the measured o.p.d. H coverage results and for the recombination mechanism.

Another important feature of the impedance spectra in Fig. 4.49 is that there is clearly no indication of a diffusion effect in the system studied. Therefore a Warburg impedance characterized by a linear Z' vs Z'' relation with unit slope (phase-angle 45°), especially at low ω , is not observed under our experimental conditions (as may be expected with a sufficiently rapidly rotated electrode), even down to 0.05 Hz. Therefore, for these measurements, the "recombination-controlled" value of $2.3 RT/2F$ (29 mV) or near for the Tafel slope does not arise under our conditions from diffusion of molecular H_2 away from the electrode surface as was proposed for active Pt electrodes by Breiter^{76,77}. (Such behaviour can, however, evidently characterize the H_2 evolution kinetics at a stationary, sufficiently active Pt electrode). In this regard,

*The linear relation between θ and η corresponds to Temkin's adsorption isotherm but the assumption of an adsorption equilibrium constant decreasing exponentially with increasing θ_H by a factor g must hold (see section 1.5.3, also ref.37-40). Except as $\theta \rightarrow 0$ or $\rightarrow 1$, such a relation gives $\theta \propto \eta$ over a potential range determined by the g value.

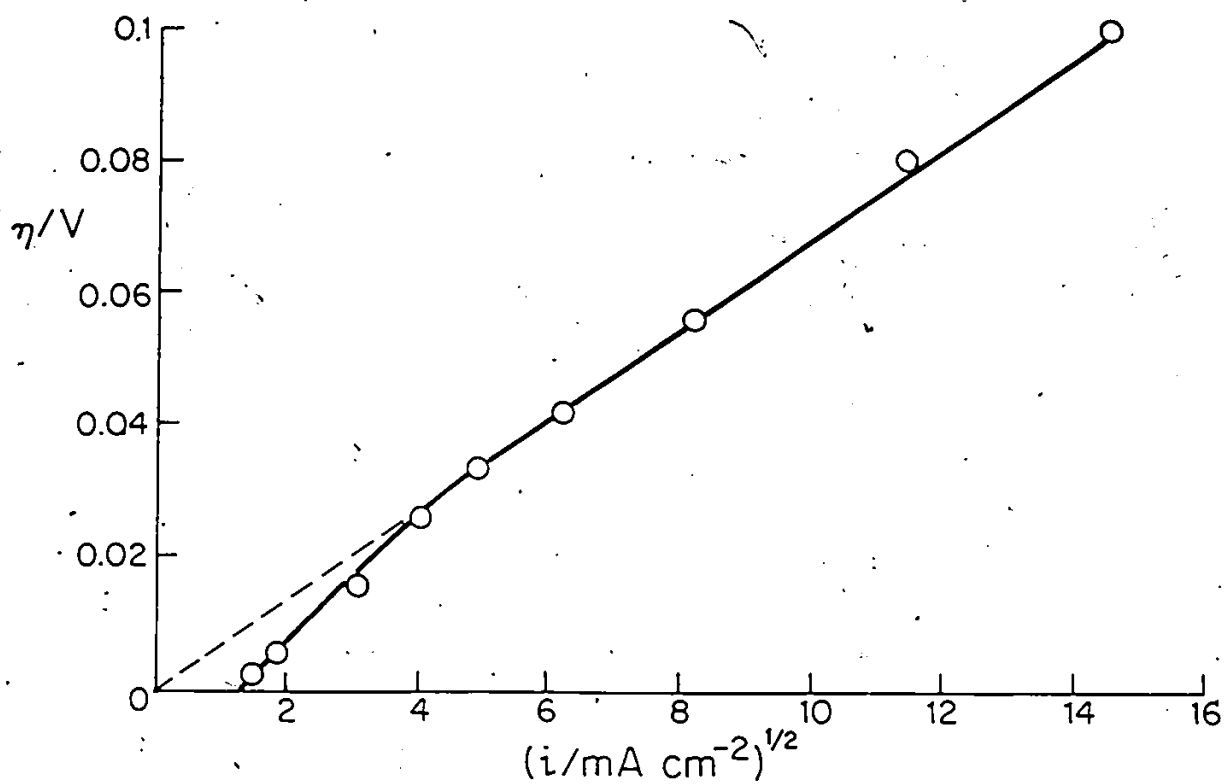


Fig. 4.52 Plots of η vs $i^{1/2}$ for the same data shown in Fig. 4.48, curve 1.

it is to be noted that the d.c. current vs potential relation and the a.c. impedance at significant cathodic overpotentials are independent of further increase of electrode rotation rate beyond ca. 3000 r.p.m. under our experimental conditions.

4.3.2.2 Unactivated Pt in 0.5 M H₂SO₄

In Fig. 4.53, curve 1 is the experimental steady-state η vs $\log i$ plot, represented by circled points, for an unactivated rotating disc Pt electrode (3600 r.p.m.). The electrode was unactivated in the sense that it had been prepolarized at $\eta = 0.1$ V cathodically for 2 h. before the a.c. impedance measurements were begun.

During this period of time, the initially active Pt electrode became poisoned by electrodeposition and/or adsorption of impurities. The effect is reproducible, in a given solution, depending on the time allowed for deactivation. This poisoning effect was observed despite the fact that high-purity techniques were used for solution preparation and cleaning of cells, as described elsewhere¹⁴⁹.

The solid line, curve (1) of Fig. 4.53, represents the numerically simulated Tafel plot based on eqn. (3.41) with rate constants taken as $k_1 = 1.8 \times 10^{-9}$; $k_{-1} = 2.5 \times 10^{-8}$; $k_2 = 3.5 \times 10^{-10}$ and $k_3 = 3.5 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1}$. Curves 2, 3 and 4 in Fig. 4.53 are η vs $\log(1/R_\infty + R_p)$, $\log(1/R_\infty)$ and $\log(1/R_p)$, plots respectively, for the experimental results (points) and the numerical simulation (solid line) based on eqn. (3.29) for the same experimental conditions and with the same set of rate constants as for curve 1 in

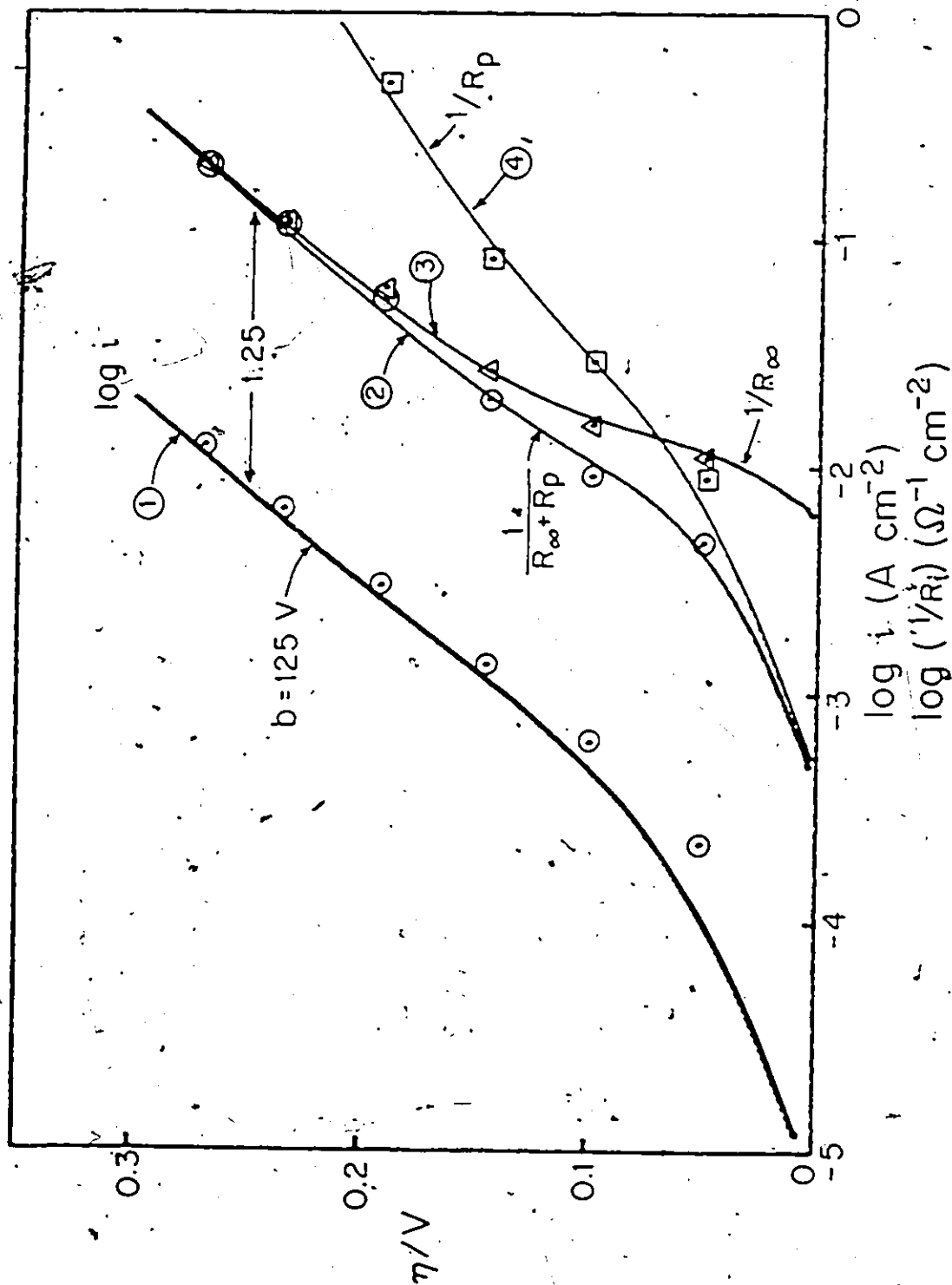


Fig. 4.53 Experimental (circled points) and simulated (solid lines) Tafel plots (curve 1) and η vs $\log(1/(R_\infty + R_p))$ (curve 2); $1/R_\infty$ (curve 3) and $1/R_p$ (curve 4) plots for the h.e.r. at unactivated Pt in 0.5 M H_2SO_4 .

Fig. 4.53 (for details, see caption of Fig. 4.53).

The Tafel plot (curve 1 in Fig. 4.53) evidently becomes a straight line with a slope of 0.125 V as $\eta > 0.15$ V which implies that the reaction rate is controlled by the electrochemical-desorption step (1.7)* with coverage of o.p.d. H approximately constant in that potential range (see Fig. 4.57). This agrees with the conclusions reached previously from the potential-decay measurements. This Tafel relation can now be expressed more precisely by the kinetic equation (3.41) using the simulation procedure.

Fig. 4.53 shows that both experimentally and by simulation, the η vs $\log i$ and η vs $\log 1/(R_{\infty} + R_p)$ plots (on the log scale - curves 1 and 2 of Fig. 4.53) become two parallel lines separated by a value of 1.25. This can be rationalized by the reaction scheme, as discussed in section 4.1.2.1, eqns. (4.14-4.16); the theoretical value should be 1.28, which is close to the experimentally observed separation value of 1.25.

This result is not surprising; because $R_{\infty} + R_p$ is the total Faradaic resistance, its reciprocal should be directly related to the Faradaic current at that potential. However, the advantage of a.c. impedance measurements is not only that they give the total Faradaic impedance, which corresponds to the steady-state Tafel plot as a description of the kinetics of the reaction

*A Tafel slope of ca. 0.125 V could also arise if the discharge step were rate-determining with o.p.d. $\theta_H \rightarrow 0$. This, however, is unlikely here since the measured θ_H is appreciably > 0 .

studied, but also, more interestingly, because R_{∞} and R_p can be evaluated separately and these quantities represent the kinetic characteristics of individual steps or a combination of them which steady-state measurements cannot provide (not to mention that a.c. impedance measurements give information also about the C_{dl} and C_p quantities).

Fig. 4.54 shows the complex-plane diagrams for a) $\eta = 0.050$, b) 0.10 , c) 0.142 and d) 0.27 V respectively. The notation on the graphs follows that in Fig. 4.49, the conditions are as for Fig. 4.53. The simulated behaviour utilizes the same set of rate constants as for Fig. 4.54 with $C_{dl} = 25 \mu F cm^{-2}$, $q_1 = 35 \mu C cm^{-2}$ and $R_s = 1.8 \Omega cm^2$.

The principal feature of the complex-plane impedance spectra in Fig. 4.54 for the unactivated Pt electrode in $0.5 M H_2SO_4$ is that they consist of two overlapping semicircles, except for the behaviour at $\eta = 0.27$ V, for which potential only an apparently single semicircle is observed. The semicircles that are resolved at the low frequency end, and which are related to R_p and C_p , become relatively smaller as η is increased. At a sufficiently high η , ($\eta = 0.27$ V), the semicircle related to the adsorption relaxation apparently completely disappears and only the semicircle related to R_{∞} and C_{dl} remains observable [see Fig. 4.54(d)]. This is consistent with the Tafel polarization behaviour (see curve 1 in Fig. 4.53), i.e. as $\eta > 0.15$ V, $d\theta/d\eta \rightarrow 0$, so that a straight line with slope $RT/6F$ (also see Fig. 4.57) should arise with no contribution from $(\partial \ln i/\partial \eta)_{\eta}$ arising from $d \ln \theta/d\eta$.

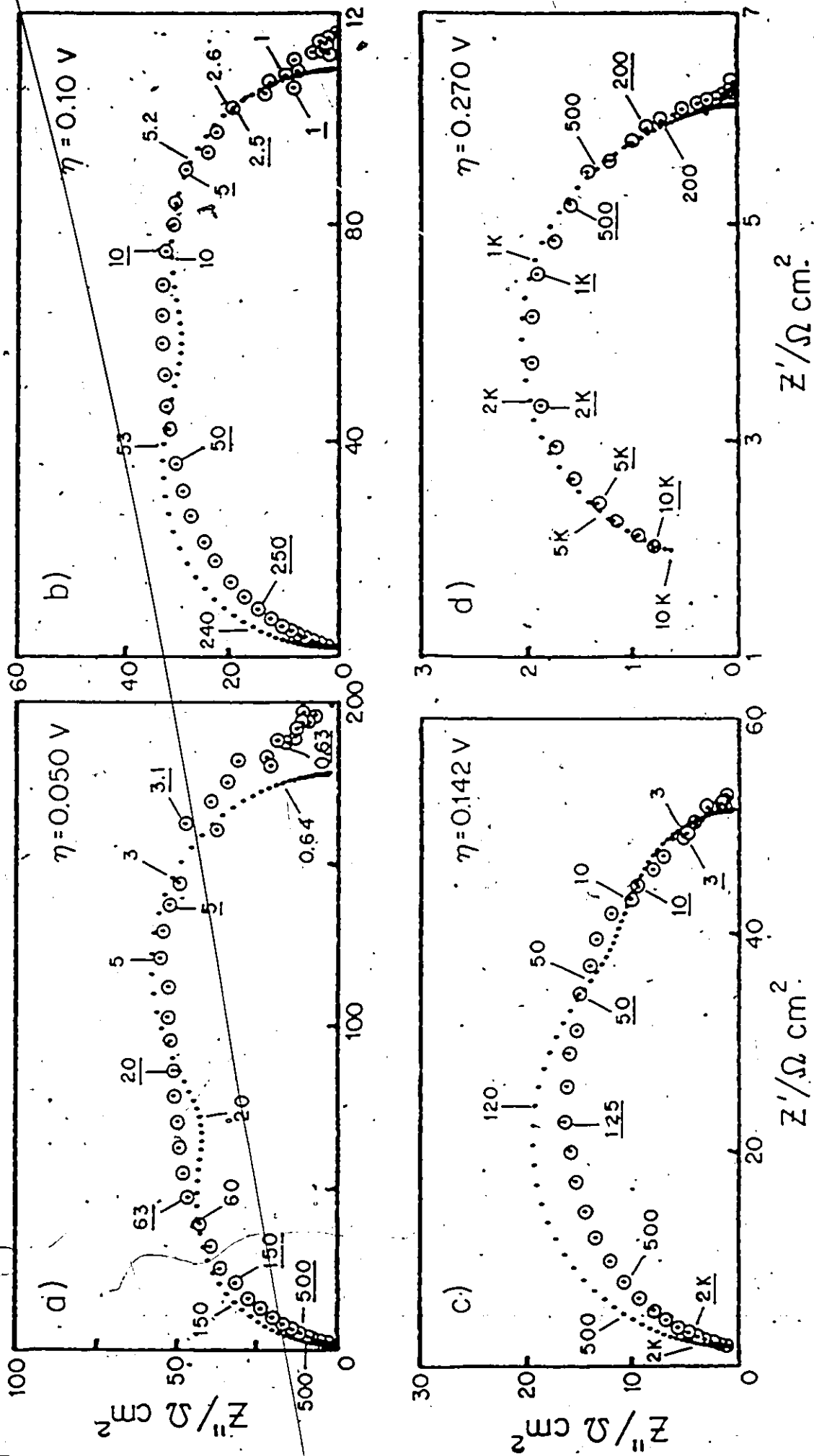


Fig. 4.54 Experimental (circled points) and simulated (points without circles) complex-plane impedance diagrams for $\eta =$ a) 0.50; b) 0.10; c) 0.142 and d) 0.270 V in the same condition as Fig. 4.53. The numbers (underlined for experimental data) indicate the respective frequencies (in Hz).

due to potential dependence of significant o.p.d. coverage.

Fig. 4.55 shows the Bode plots for unactivated Pt in 0.5 M H_2SO_4 . The experimental conditions and theoretical parameters for curves 1, 2, 3 and 4 in Fig. 4.55 are the same as for curves a, b, c and d in Fig. 4.54. It is seen that the simulated behaviour (solid line in Fig. 4.55), provides a good fit to the experimental data (points in Fig. 4.55).

A dramatic difference is that the value required for q_1 is now quite small ($\approx 35 \mu\text{C cm}^{-2}$) at the unactivated Pt electrode instead of $q_1 = 2300 \mu\text{C cm}^{-2}$ for activated Pt in 0.5 M H_2SO_4 . Only with such a low q_1 value does the simulated frequency dispersion of the impedance spectra give a good fit to the experimental behaviour.

This is seen in Fig. 4.56, which shows the simulated impedance spectra in the complex-plane for the same conditions as for Fig. 4.54(a), except $q_1 = 25, 50, 100$ and $210 \mu\text{C cm}^{-2}$ are taken for curves 1, 2, 3 and 4, respectively. For $q_1 = 210 \mu\text{C cm}^{-2}$, as usually assumed, the impedance spectrum consists of two "separated" semi-circles (curve 4, Fig. 4.56); which differ from the observed "over-lapping-circle" type impedance spectra. It is clear that the "overlapping-circle" impedance spectra can only be simulated with small q_1 values (curves 1, 2 in Fig. 4.56) in the Langmuir isotherm case, $g = 0$; the behaviour when $g \neq 0$ (lateral interaction case) will be discussed in section 4.3.2.6.

The small q_1 value is also consistent with the small capacitance values that are calculated approximately from the top points

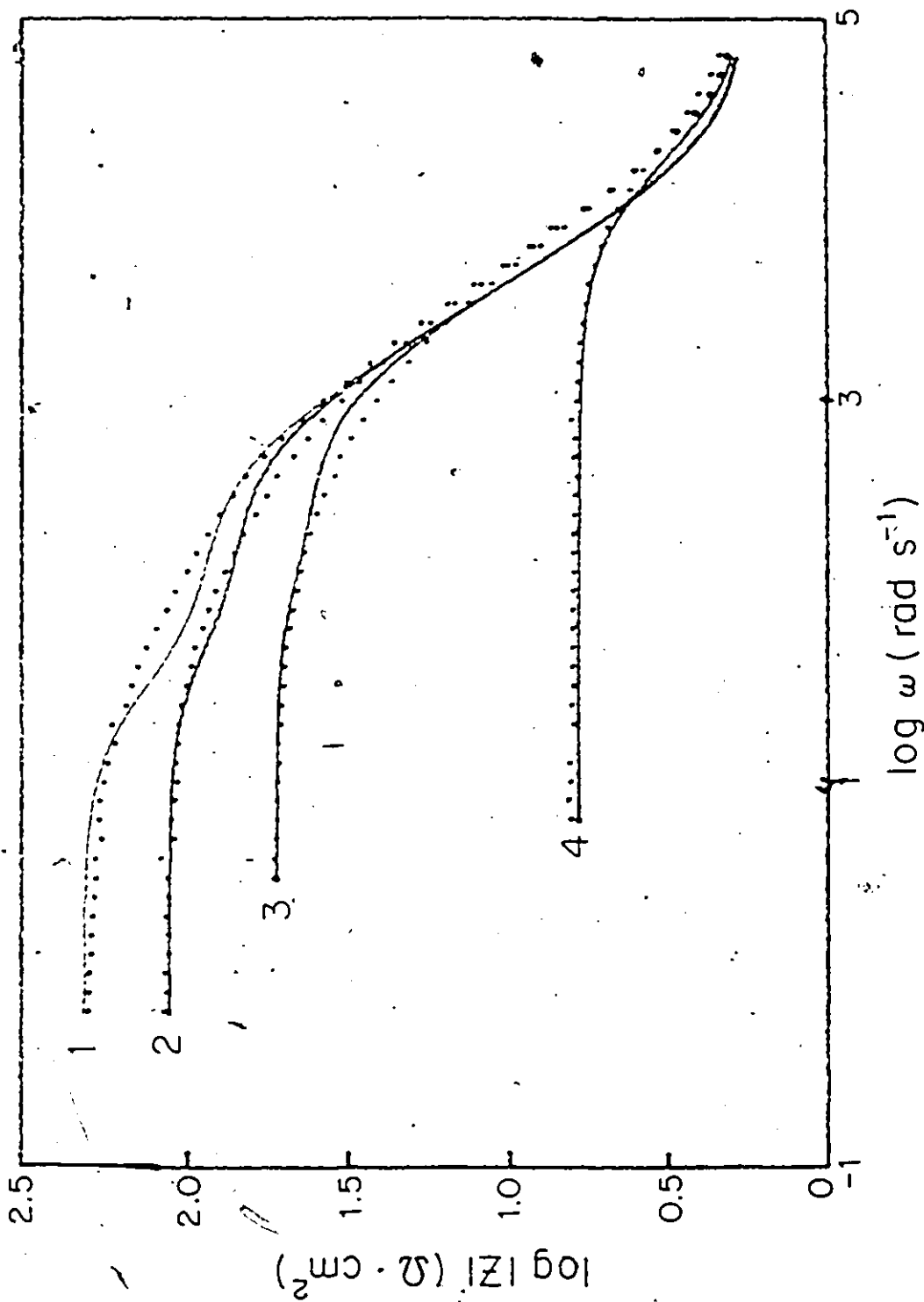


Fig. 4.55 Experimental (points) and simulated (solid lines) Bode plots for h.e.r. at unactivated Pt in 0.5 M H_2SO_4 . The experimental conditions and theoretical parameters for curves 1, 2 3 and 4 are the same as those for diagrams a, b, c and d in Fig. 4.54.

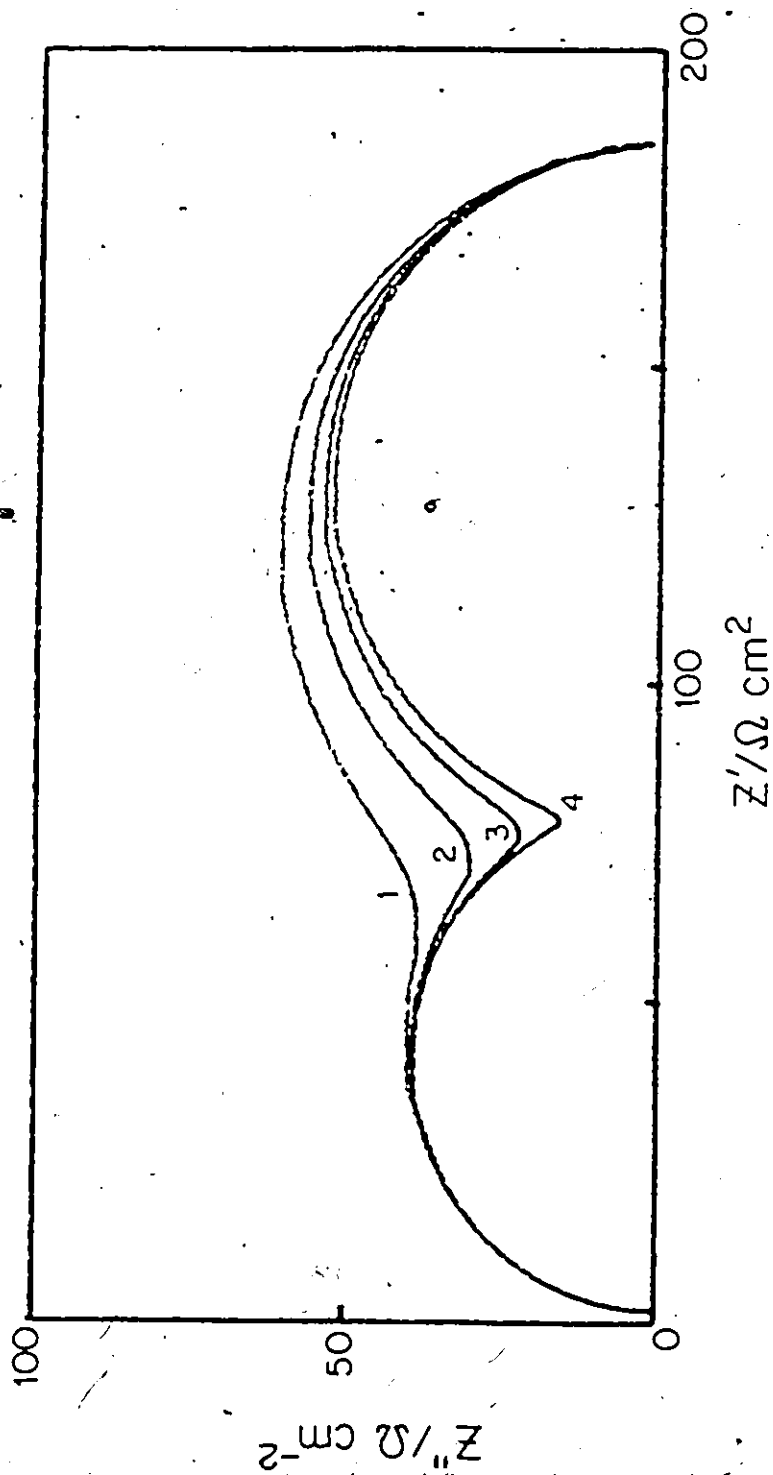


Fig. 4.56 Simulated impedance spectra in the complex-plane for the same conditions as for Fig. 4.54(a) except $q_1 = 25, 50, 100$ and $210 \mu\text{C cm}^{-2}$ are taken for curves 1, 2 3 and 4, respectively.

of the adsorption C_p semicircles, i.e. at the low frequency end of the impedance spectra. For example, at $\eta = 0.050$ V (see Fig. 4.54(a)), C_p is ca. $260 \mu F cm^{-2}$.

The simulated C_ϕ , C_p , θ_H and τ vs η plots, using the same values of the rate constants and parameters as in Figs. 4.53 and 4.54, are shown in Fig. 4.57; it can be seen that the C_ϕ and τ curves have similar shapes; these are the quantities (see section 3.2) that are directly related to the adsorption of o.p.d. H. C_p exponentially increases over the whole potential range, reaching a value of $12 mF cm^{-2}$ at $\eta = 0.3$ V. Comparing the curve for C_ϕ with that for C_p , it may be concluded that C_p does not have the usual significance of a steady-state adsorption pseudocapacitance in this case.

Since, from u.p.d. measurements, full coverage of strongly bound H is known to correspond to a charge of $210 \mu C cm^{-2}$ (for Pt (111)), the present result for $q_1 = 35 \mu C cm^{-2}$, for the o.p.d. H represents only a 17% extra coverage, i.e. only this fraction of sites are electro-active for cathodic H_2 evolution involving the o.p.d. H. Measurements by cyclic-voltammetry gave a charge for u.p.d. H corresponding to ca. 20% coverage after 1 h polarization. These results lead to the same conclusion as our potential-relaxation method (see section 4.3.1.3), i.e., poisoning effects on the kinetic activity of Pt electrodes for the h.e.r. are directly related to the effects of accumulated adsorbed impurities on the active sites on Pt surface which reduce the coverage of both the o.p.d. and u.p.d. H.

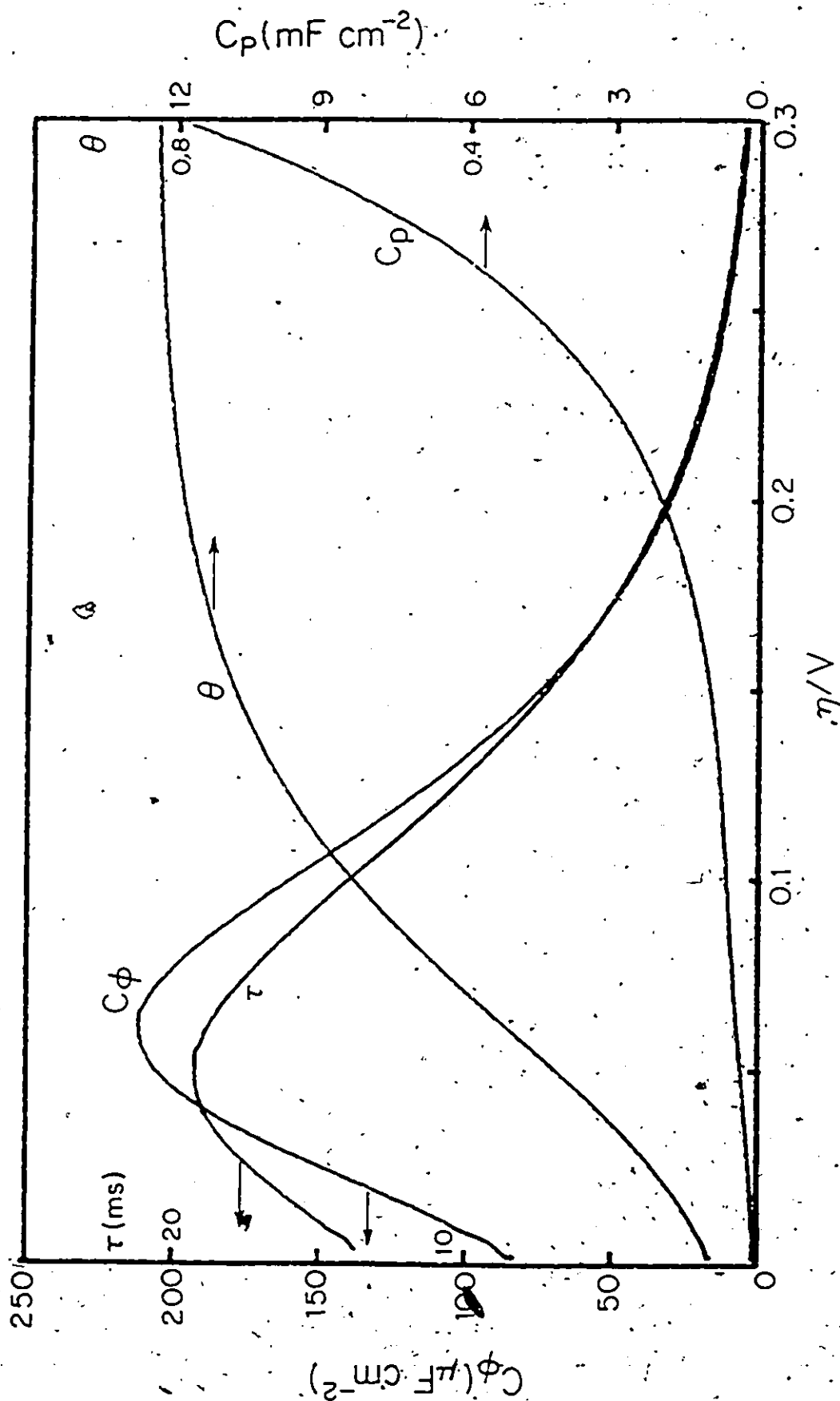


Fig. 4.57: Simulated C_ϕ , C_p , θ_H and τ vs η plots, using the same values of the rate constants and parameters as in Figs. 4.53 and 4.54.

Comparison of the rate constants for the unactivated Pt⁴ with those for activated Pt, both in acid solution, shows that after 2 h cathodic polarization, the activated Pt became appreciably "poisoned" and the values of k_1 , k_{-1} , k_2 and k_3 required to represent the polarization and the impedance behaviour of the electrode become respectively 571, 640, 85 and 1140 times smaller. The most significant change is that k_3 becomes much smaller, i.e. the recombination contribution to the desorption process is much attenuated.

The information above leads to a clear picture concerning what happens on a Pt electrode surface in going from the "activated" to an "unactivated" state: when an activated Pt electrode is cathodically polarized, impurities become deposited and/or adsorbed on active sites of the Pt surface, leading to reduction of the parameters k_1 , k_{-1} and q_1 . Correspondingly, coverage of o.p.d. H is decreased and the parameters k_2 , k_3 are reduced. Especially k_3 suffers a dramatic decrease because the recombination step is only favoured as the principal desorption pathway on the Pt surface when the o.p.d. H coverage is high, as was concluded also from the potential decay work (section 4.3.1).

Since most impurities on the surface can be anodically oxidized and removed into solution, the Pt electrode can be easily reactivated by such a treatment, as is well known.

4.3.2.3 Activated Pt in 0.5 M NaOH

In Fig. 4.58, curve 1 is the steady-state polarization η vs $\log i$ plot. The points with circles in curve 1 are the experimental-

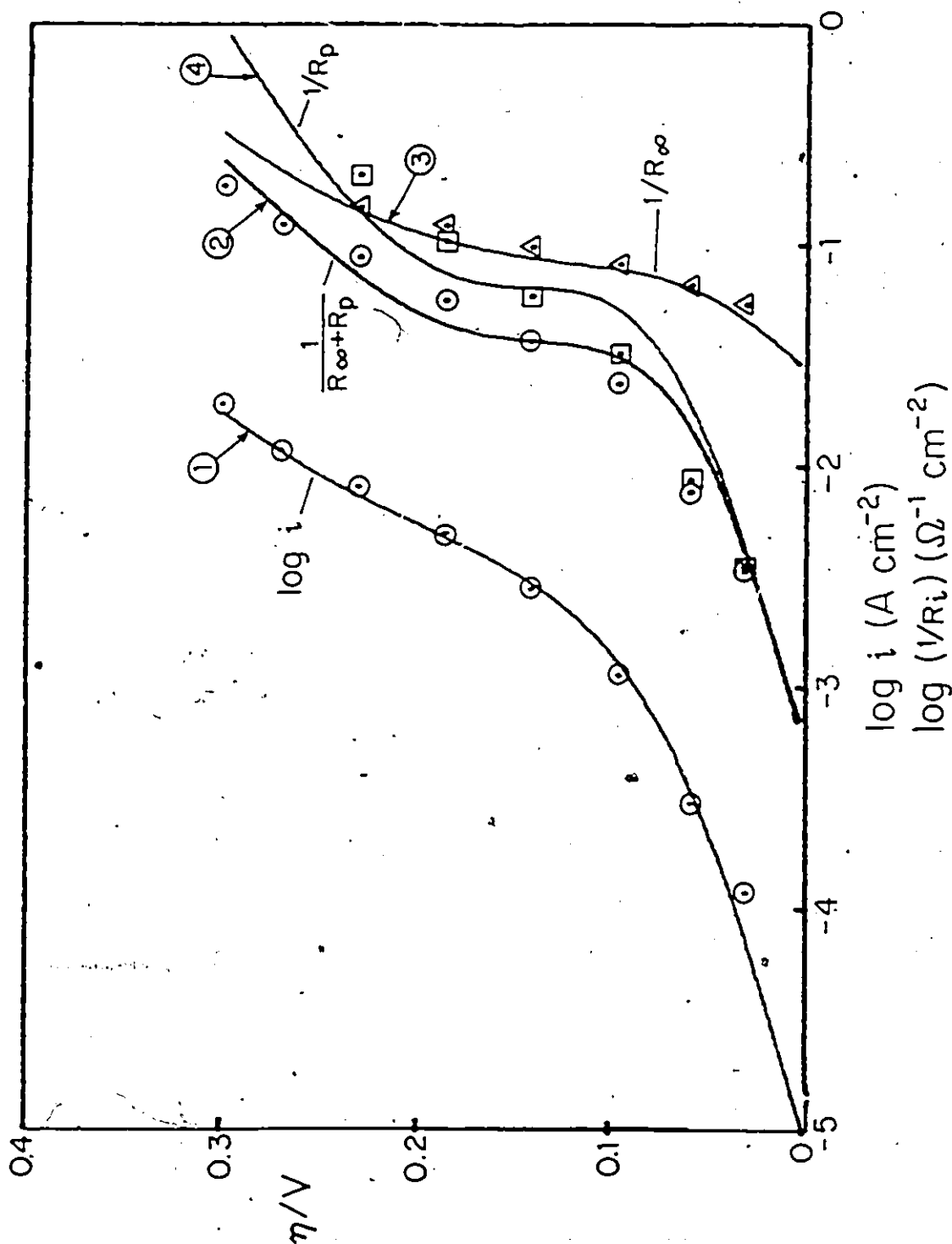


Fig. 4.58 Experimental (points) and simulated (solid lines) Tafel plots (curve 1) and η vs $\log(1/R_\infty + R_p)$ (curve 2); $1/R_\infty$ (curve 3) and $1/R_p$ (curve 4) plots for the h.e.r. at activated Pt in 0.5 M NaOH solution.

ly measured data obtained in 0.5 M NaOH at the activated Pt rotating disc electrode (3600 r.p.m.) while the solid line of the curve 1 is the simulated Tafel plot based on eqn. (3.41) with the rate constants taken as follows: $k_1 = 0.8 \times 10^{-8}$; $k_{-1} = 5 \times 10^{-8}$; $k_2 = 2 \times 10^{-10}$; $k_3 = 2.5 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}$. The concentration term involved in the kinetic equations differs, of course, for acidic and alkaline solutions for the h.e.r. As in Figs. 4.48 and 4.53, curves 2, 3 and 4 in Fig. 4.58 are the η vs $\log (1/(R_\infty + R_p))$, $\log (1/R_\infty)$ and $\log (1/R_p)$ plots, respectively, for the experimental results and the numerically simulated behaviour based on eqns. (3.42) for the same experimental conditions and with same rate constants as for curve 1 in Fig. 4.58 (for details, see caption of Fig. 4.58).

The ratio k_3/k_2 required to account for the results is 125, which again indicates that it is the recombination step that principally characterizes the kinetic behaviour at low η (or the case of the activated electrode. This is in agreement with the conclusion from our previous observations, under the same conditions, using the potential relaxation method (see section 4.3.1.5).

Fig. 4.59 shows the complex-plane impedance diagrams for $\eta =$ a) 0.030, b) 0.060, c) 0.142 and d) 0.29 V, respectively. The notation on these graphs again follows that in Fig. 4.54. The conditions are as for Fig. 4.58. The same set of rate constants was used for the simulated curves as for Fig. 4.58, taking $C_{dl} = 25 \mu\text{F cm}^{-2}$, $q_1 = 70 \mu\text{C cm}^{-2}$ and $R_s = 3.7 \Omega \text{ cm}^2$, as found experimentally.

Again, the impedance spectra in Fig. 4.59 for the h.e.r., at the activated Pt in 0.5 M NaOH consist of two overlapping

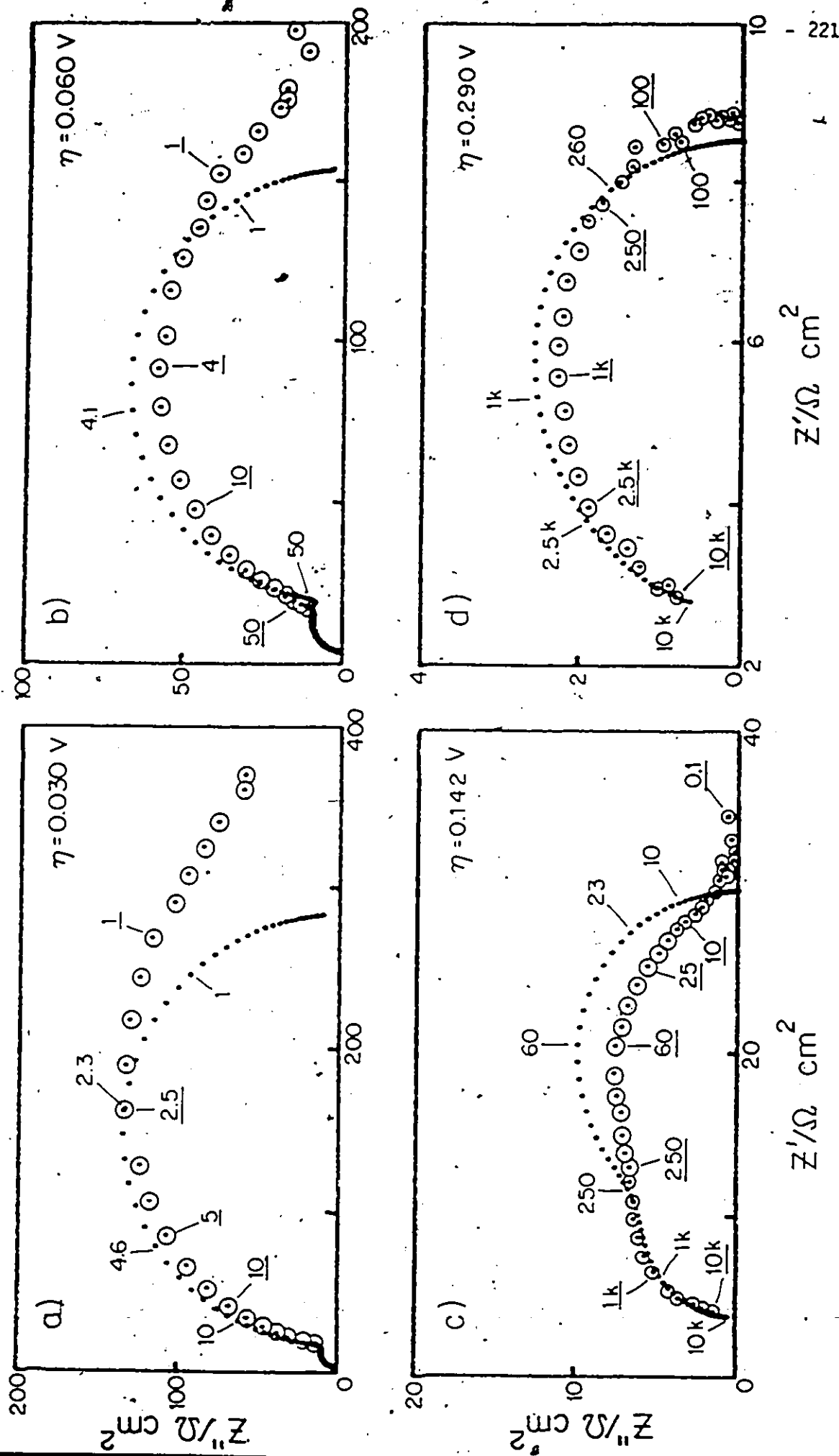


Fig. 4.59 Experimental (circled points) and simulated (points without circles) complex-plane diagrams for $\eta =$ a) 0.030; b) 0.060; c) 0.142 and d) 0.290 V for the same conditions as in Fig. 4.58. The numbers (underlined for experimental data) indicate the respective frequencies (in Hz).

semicircles; the relative size of the semicircle for the high frequency end increases with η . The capacitance value for this semicircle corresponds to C_{dl} and can be simulated by our model and evaluated approximately for the top points of the semicircles at each η and gives a constant value, $25 \mu F cm^{-2}$, as found for the other systems treated in sections 4.3.2.1 and 4.3.2.2. Also, only for C_{dl} taken as ca. $25 \mu F cm^{-2}$ do the simulated impedance diagrams provide a best fit to the observed frequency dispersion of the experimental impedance data (also see Fig. 4.60). The value of the $C_{dl} = 25 \mu F cm^{-2}$ is in good agreement with the value ($C_{dl} = 25 \mu F cm^{-2}$) determined from the potential relaxation method (see Figs. 4.40b and 4.41b).

Fig. 4.59 shows that the impedance diagrams have a descending tail at the low frequency ends and for small η 's. These tails can not be explained by the influence of a Warburg impedance component corresponding to a diffusion effect because the tails become smaller as η is increased and, at $\eta = 0.29 V$, eventually completely disappear. Contrarily, if this effect was due to diffusion, the tails should become more and more significant with increasing η and also have a positive rather than a negative slope in the Z' vs Z'' plots.

One possible explanation for the appearance of a tail at low frequencies is the formation of a hydride in the region of the Pt surface which becomes saturated with H at high η^* . The charge for

*In connection with this suggestion that is reluctantly proposed, it is to be noted that Gileadi, Fullenweider and Bockris¹⁹² observed sorption into Pt that was not associated, they claimed, with H migration into grain boundaries.

formation of the hydride is higher compared with that for adsorbed H on the surface, and gives rise to the larger capacitance at low frequency than that for the 2-d chemisorbed H.

The value of q_1 for best fit of the behaviour at activated Pt in 0.5 M NaOH is $70 \mu\text{C cm}^{-2}$ (see also Fig. 4.60). This implies that only 33% of Pt surface atoms behave as "active sites" for the o.p.d. H, as also concluded from the potential-relaxation experiments for the same conditions (see section 4.3.1.3 b), where the total charge for o.p.d. H was found to be $80 \mu\text{C cm}^{-2}$, i.e. for 38% of total sites being utilized.

Hence, the Pt electrode is a much poorer electrocatalyst for the h.e.r. in alkaline than in acidic solution, not only because the activation energy for proton discharge is higher from H_2O than H_3O^{+} , but also because a smaller fraction of Pt sites is being utilized for o.p.d. of H in the reaction.

Fig. 4.60 shows the Bode plots for the same experimental data together with simulated results as shown in the complex-plane plots of Fig. 4.59 a. Fig. 4.60a shows a plot of $\log |z|$ vs $\log \omega$ while in Fig. 4.60b the phase is plotted vs $\log \omega$. It can be seen that the numerically simulated curve for $q_1 = 70 \mu\text{C cm}^{-2}$ (solid line 2 in Fig. 13a and solid line in Fig. 4.60b) gives a good fit to the experimental data (points with circles) except for a few points at very low frequency which correspond to the tail in Fig. 4.59a. This region may correspond to a further capacitance associated with a slow relaxation due to hydride formation as was also indicated at Ni-Mo hydrogen cathodes (see section 4.1.2.2).

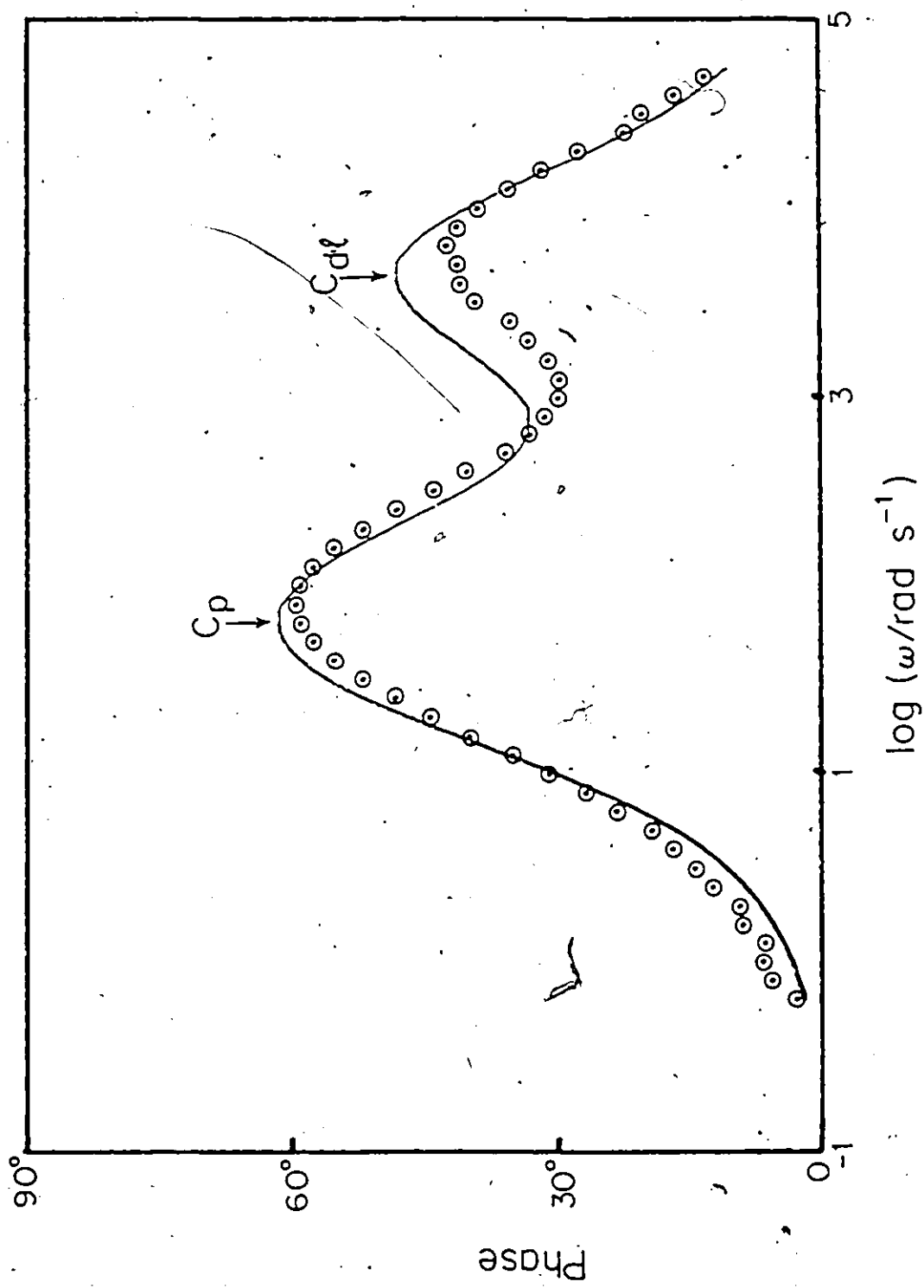


Fig. 4.60(a) Experimental (circled points) and simulated (solid lines) Bode plots for the h.e.r. at activated Pt in 0.5 M NaOH solution at $E = 0.030$ V (same data and rate constants as in Fig. 4.59(a)). Diagram a is the phase vs log ω while b is the log $|Z|$ vs log ω plots. (b see next page).

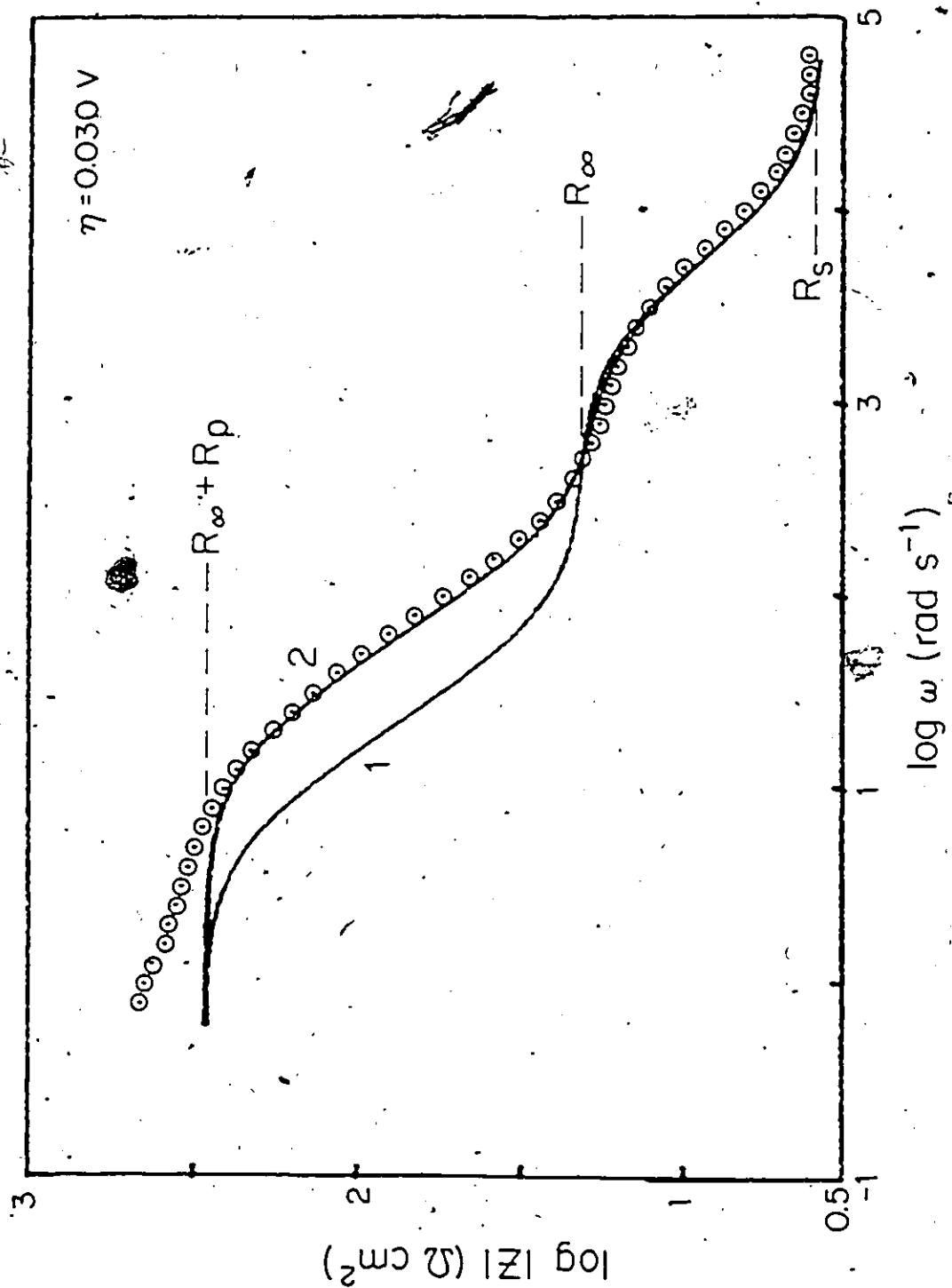


Fig. 4.30 (b)

As an illustration of the requirement that q_1 have a value of ca. $70 \mu\text{C cm}^{-2}$, a calculated Bode plot taking $q_1 = 210 \mu\text{C cm}^{-2}$ is also shown in Fig. 4.60 (solid line 1); the results are obviously not fitted by such a value. Fig. 4.60 provides a good illustration of the value of a Bode plot giving information about $R_\infty, R_p, R_s, C_{dl}$ and C_p (for details see caption of Fig. 4.60).

Fig. 4.61 shows the simulated curves of η vs $C_\phi, C_p, \theta_H, \tau$ numerically calculated for the same set of rate constants and parameters as for Fig. 4.59. Again the τ and C_ϕ curves have similar shapes and C_p has a higher peak value but a similar shape to that of C_ϕ vs η for $\eta < 0.2 \text{ V}$, as with activated Pt in acidic solution.

4.3.2.4 Unactivated Pt in 0.5 M NaOH

We follow the presentation in earlier sections; thus in Fig. 4.62, curve 1 is the steady-state polarization η vs $\log i$ plot. The points with circles in curve 1 represent the experimental results in 0.5 M NaOH at an unactivated Pt rotating-disc electrode (3600 r.p.m.), which was pre-polarized cathodically at $\eta = 0.1 \text{ V}$ for one hour before the a.c. impedance measurements were commenced, while the solid line of curve 1 represents the numerically calculated η vs $\log i$ plot from eqn. (3.41) with rate constants taken as $k_1 = 1.5 \times 10^{-10}$, $k_{-1} = 0.4 \times 10^{-10}$, $k_2 = 2.2 \times 10^{-11}$ and $k_3 = 2.5 \times 10^{-10} \text{ mol cm}^{-2} \text{ s}^{-1}$, for β taken as 0.48. Curves 2, 3 and 4 in Fig. 4.62 are the plots of η vs $\log 1/(R_\infty + R_p)$, $\log 1/R_\infty$, and $1/R_p$, respectively, for the experimental results (points) and

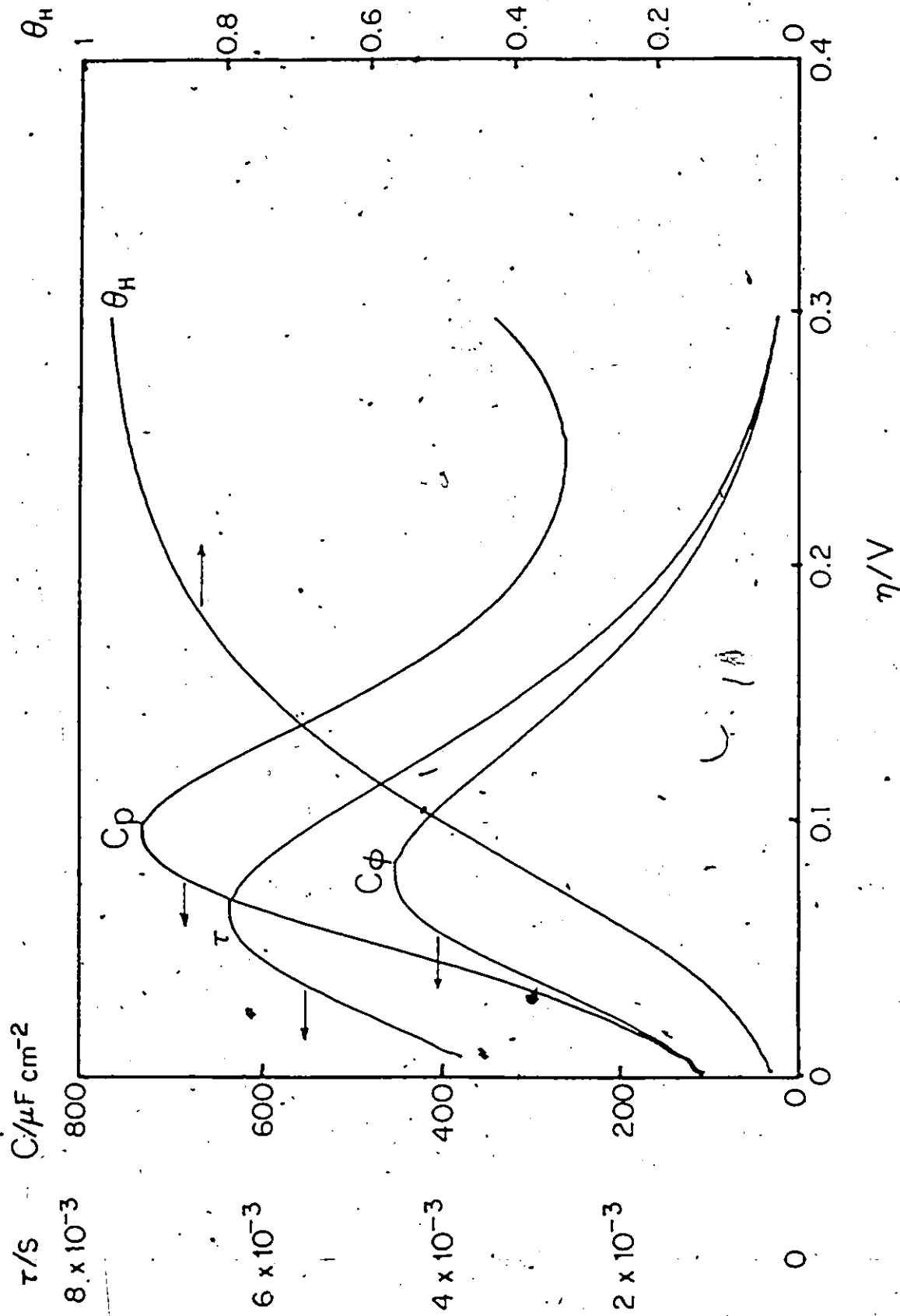


Fig. 4.61 Simulated curves of η vs C_ϕ , C_p , θ_H and τ numerically calculated for the same set of rate constants and other parameters as for Fig. 4.59.

numerically simulated behaviour (solid lines) using eqn. (3.29) for the same experimental conditions and with the same parameters as for curve 1 in Fig. 4.62.

For the same reason as was discussed in section 4.2.3.2 for unactivated Pt in acid, the Tafel and η vs $\log 1/(R_{\infty} + R_p)$ plots become two parallel straight lines separated by a distance of 1.24 when $\eta > 0.15$. This also implies that the reaction is controlled by the electrochemical-desorption step (1.7) with o.p.d. H coverage $\theta_H \gg 0$ and almost constant when $\eta > 0.15$ V, as was found in the case of the Ni electrode in alkaline solution (see section 4.1.1).

Fig. 4.62 shows that the Tafel plot bends down from the straight line section at low η values, which is unusual. A Tafel plot like this can arise when θ_H is relatively high ($\theta_{\eta=0} \gg 0$) at low η . The simulated behaviour of this system gives a good fit to both the θ vs η (see Fig. 4.65) and the Tafel relations (see Fig. 4.62 curve 1).

Fig. 4.62 shows that R_{∞} is the main component of the total impedance, i.e., $R_{\infty} \gg R_p$, even at low η . This implies that the coverage by o.p.d. H is small. A similar situation ($R_{\infty} \gg R_p$) is encountered in the study of the h.e.r. at the Ni electrode in alkaline solution (see section 4.2.1 and Fig. 4.18).

Fig. 4.63 shows the complex-plane impedance diagrams for $\eta =$ a) 0.050, b) 0.15, c) 0.20 and d) 0.39 V, respectively. The results are represented in the same way as for other cases (Figs. 4.49, 54 and 59). The parameters used for the simulation curves

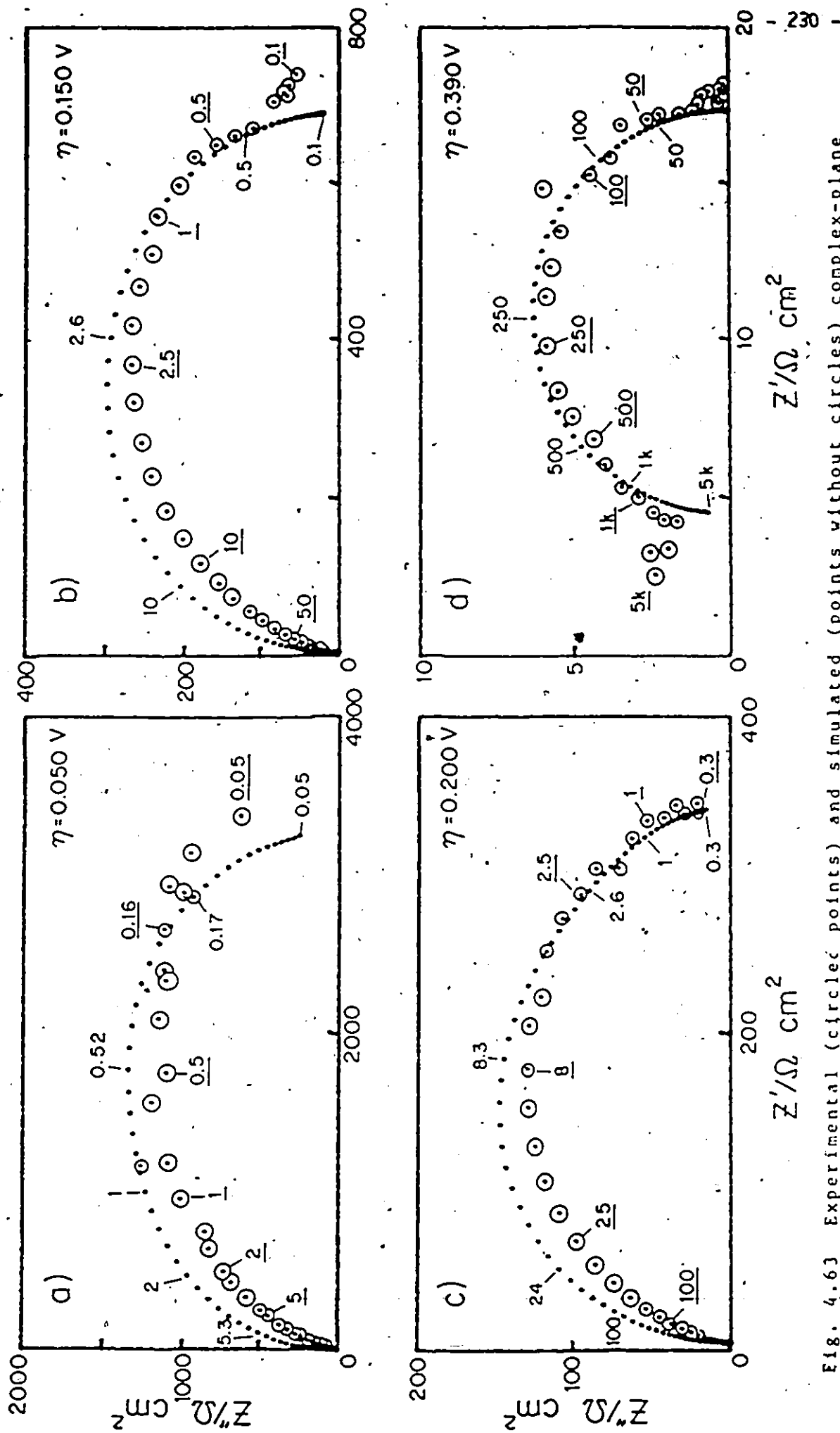


Fig. 4.63 Experimental (circled points) and simulated (points without circles) complex-plane diagrams for $\eta =$ a) 0.050; b) 0.150; c) 0.20 and d) 0.390 V in the same condition as in Fig. 4.62. The numbers indicate the respective frequencies (in Hz).

are $\beta = 0.48$, $q_1 = 20 \mu\text{C cm}^{-2}$, $C_{dl} = 50 \mu\text{F cm}^{-2}$ and $R_s = 4.5 \Omega$, and rate constants are the same as for Fig. 4.62.

The symmetry factor $\beta = 0.48$ corresponds to the slightly high Tafel slope, $b = 0.128 \text{ V}$ (Fig. 4.62, curve 1). The required double-layer capacitance ($50 \mu\text{F cm}^{-2}$) is a little higher than for the three previous cases.

The lowest q_1 value ($20 \mu\text{C cm}^{-2}$), which implies that only ca. 10% of Pt atoms on the electrode surface are "active", is related to the unactivated Pt electrode in alkaline solution having the poorest electrocatalytic activity for the h.e.r. among the four systems studied (compare the rate constants or Tafel plots for the four systems; Table 4.5).

Most of the impedance spectra in Fig. 4.63 (a, b, c) consist of two unresolved overlapping semicircles except diagram (d) for $\eta = 0.39 \text{ V}$ which is a single semicircle corresponding to the impedance of the combination of C_{dl} and R_∞ . The experimental and calculated frequency dispersions of the impedance spectra in Fig. 4.63, like the ones for other systems, are in good agreement with each other. This is demonstrated by the Bode plots shown in Fig. 4.64 (compare Fig. 4.55). Curves 1, 2, 3 and 4 in Fig. 4.64 represent the same results as those of diagrams a, b, c and d, respectively, in the complex-plane plots of Fig. 4.63.

The simulated C_ϕ , C_p , θ_H and τ vs η plots for unactivated Pt in 0.5M NaOH are shown in Fig. 4.65. The situation here is very similar to the case in 0.5M H_2SO_4 (see p. 216 and Fig. 4.57).

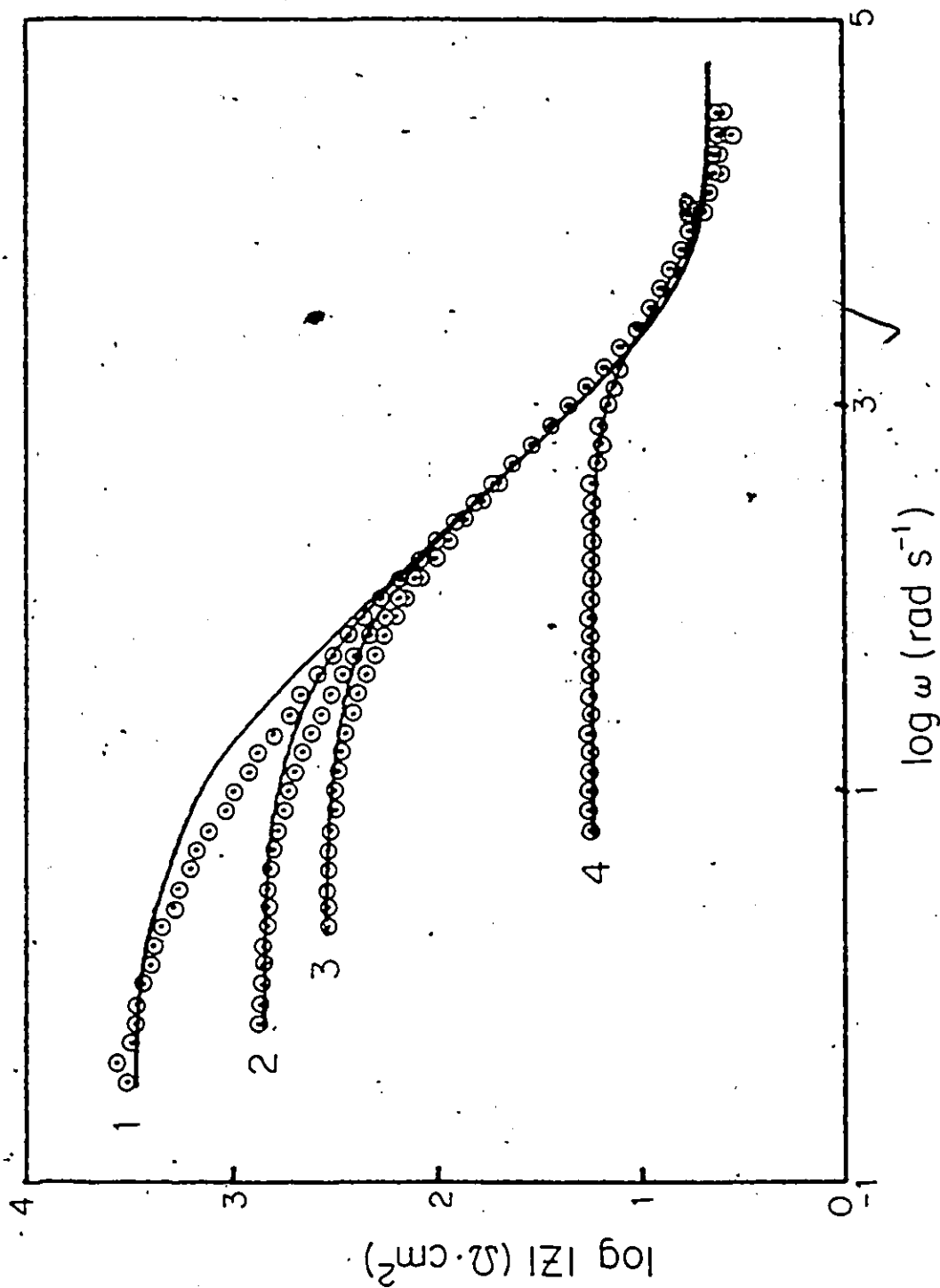


Fig. 4.64 Experimental (circled points) and simulated (solid lines) Bode plots for h.e.r. at unactivated Pt in 0.5 M NaOH solution. The experimental data and theoretical parameters for curves 1, 2 3 and 4 are the same as those for diagrams a, b, c and d in Fig. 4.63.

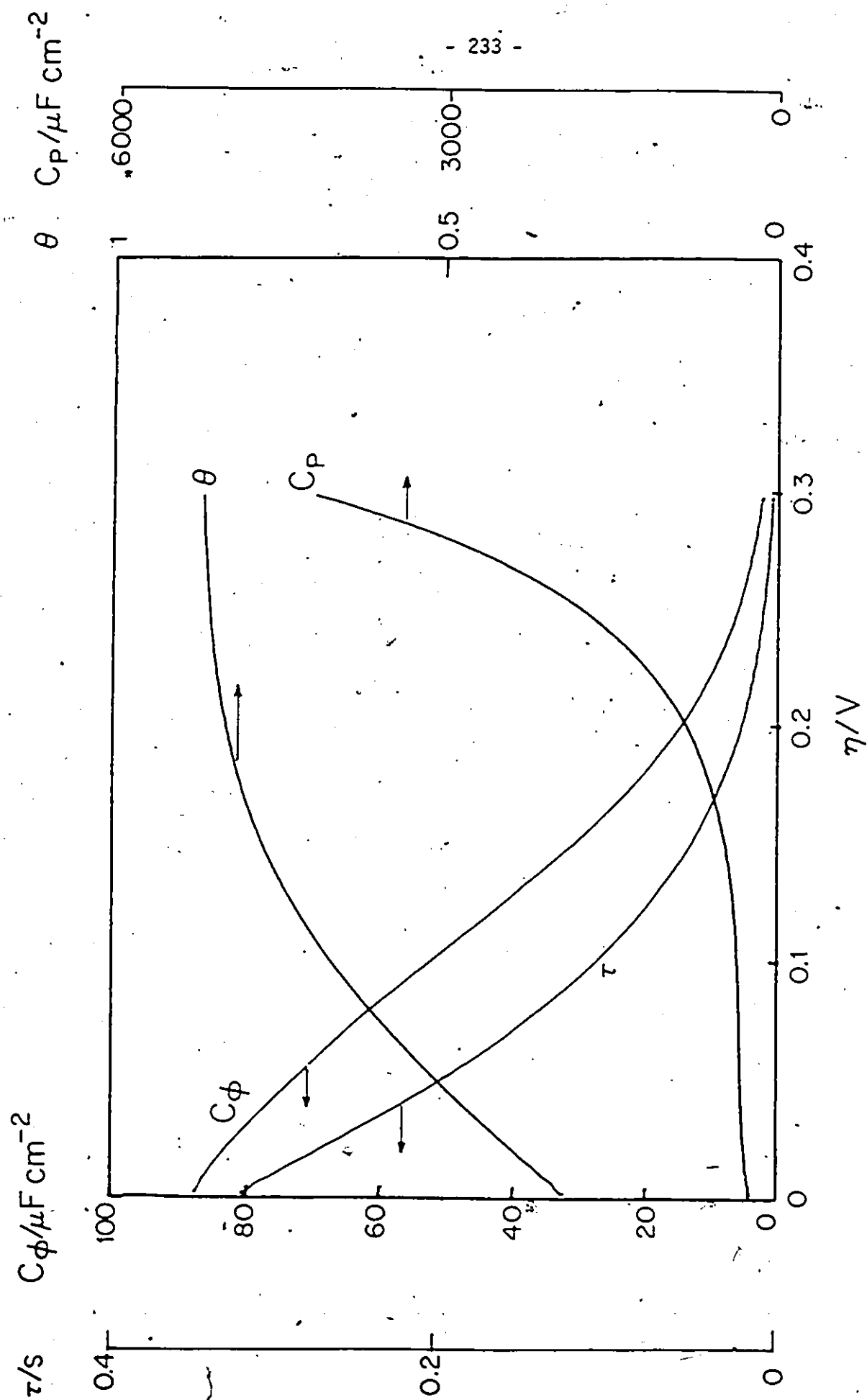


Fig. 4.65 Simulated curves of η vs C_ϕ , C_p , θ_H and τ numerically calculated for the same set of rate constants and other parameters as for Fig. 4.63.

4.3.2.5 Summary of values of the rate constants required for simulation of the h.e.r. kinetics at Pt

The rate constants for the four systems studied are listed together in Table 4.5*. The q_1 values and corresponding data on o.p.d. H coverage in terms of "equivalent monolayers" derived both from the a.c. impedance measurements and the potential-relaxation method are also recorded in Table 4.5.

The exchange current-density, i_0 , is a widely used measure of the electrocatalytic activity of an electrode for a particular process. However, it contains various factors such as H coverage, the rate constants for participating steps, etc. that cannot be distinguished. On the contrary, the rate constants listed in Table 4.5 describe, for the first time, each step individually and quantitatively for certain reaction mechanisms; moreover, the steady-state coverage as a function of η can be calculated for the mechanism using the rate constant values. Therefore, the current for the individual steps can be evaluated as $f(\eta)$.

From the a.c. impedance measurements, the rate constants for the h.e.r. at the Pt electrode decrease in the order; activated in H_2SO_4 , activated in NaOH, unactivated in H_2SO_4 and unactivated in NaOH, while the charge for o.p.d. H coverage decreases in the same order, i.e., the electrocatalytic activity of Pt for the h.e.r. is closely related to the extent of o.p.d. H adsorption on the electrodes, as was concluded for the same systems using the potential-relaxation method (see section 4.3.1.4).

*The rate constants for unactivated Pt are only significant for comparison with the results for activated Pt. Since the Pt de-activation depends on the polarization time, cleanness of solution and pretreatment of electrodes, the rate constants also depend on these factors and could be changing all the time.

Table 4.5 Summary of the rate constants and q_1 for the four systems.

System	k in $\text{mol cm}^{-2} \text{s}^{-1}$				q_1 (full-coverage charge) $\mu\text{C cm}^{-2}$	OPD H coverage *	
	k_1	k_{-1}	k_2	k_3		for a.c. impedance	for potential-decay **
act. Pt in 0.5 M H_2SO_4	1×10^{-6}	1.6×10^{-5}	3×10^{-8}	4×10^{-6}	2300	11	8.8
act. Pt in 0.5 M NaOH	0.8×10^{-8}	5×10^{-8}	2×10^{-10}	2.5×10^{-8}	70	0.33	0.38
U-A Pt in 0.5 M H_2SO_4 (after 2.5h)	1.8×10^{-9}	2.5×10^{-8}	3.5×10^{-10}	3.5×10^{-9}	35	0.17	
U-A Pt in 0.5 M NaOH (after 1h)	1.5×10^{-10}	0.4×10^{-10}	2.2×10^{-11}	2.5×10^{-10}	20	0.1	0.1

* Assuming the H deposition charge for a monolayer is $210 \mu\text{C cm}^{-2}$.

** See section 4.3.1.

4.3.2.6 Simulation of the kinetic behaviour for $g \neq 0$

In the simulations described above, the q_1 values were varied to fit the experimental impedance frequency dispersion, taking the Langmuir adsorption isotherm ($g=0$). Since a finite lateral-interaction factor, g (see eqn. 1.14); also could influence the impedance spectra, the situation of $g \neq 0$ must be considered.

Since an exponential dependence of K on θ is usually assumed, it may reasonably be extended to a corresponding dependence of rate constants on coverage³⁷⁻⁴⁰.

Thus, the rate of an adsorption step will decrease while that of a desorption step will increase with increasing θ_H through the factor g . Following similar treatments to those in section 3.2, the steady-state coverage θ_H and pseudocapacitance, C_ϕ , can be obtained by numerical solution of the equation (taking $\theta = 0.5$)

$$2\theta_H^2 l_3 \exp(g\theta/2) - l_1(1-\theta_H)\exp(-g\theta_H) + \theta_H(l_{-1}+l_2) = 0 \quad (4.24)$$

and corresponding a.c. impedance spectra can also be numerically simulated through introduction of coverage-dependent rate-constants.

The numerical fitting of experimental data in terms of different g values was carried out. For example, the results for unactivated Pt in 0.5 M H_2SO_4 will be shown here.

The experimental impedance complex-plane plots (as in Fig. 4.54) could be approximately fitted with $q_1 = 210 \mu C \text{ cm}^{-2}$, $C_{dl} = 25 \mu F \text{ cm}^{-2}$ and $g = 5$ with $k_1 = 3 \times 10^{-9}$, $k_{-1} = 1 \times 10^{-8}$, k_2

2×10^{-10} and $k_3 = 4 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1}$. The θ_H and C_ϕ vs η profiles calculated with these parameters are shown in Fig. 4.66a and b, respectively. When $g > 0$, the capacitance peaks decrease in height and spread over a greater potential range as has also been shown for the u.p.d. behaviour³⁸ (the o.p.d. behaviour is somewhat different from that discussed in ref. 38, since a pathway of two parallel desorption steps (eqns. 1.7 and 1.8) is assumed in the present cases).

However, with the same parameters as above, the simulated $\log i$ and $\log (1/(R_\infty + R_p))$ vs η profiles are two parallel lines separated by a distance 1.86 (Fig. 4.67), instead of the experimentally measured value of 1.25 (see Fig. 4.53). This may be explained as follows: since θ_H does not reach a constant value, even at $\eta = 0.3 \text{ V}$, when $g = 5$, eqn. (4.16) becomes

$$\log(1/R_\infty + R_p) = \log i + \log (BF/RT) + A \quad (4.25)$$

where A is proportional to $dk(\theta)/d\eta$ and $d\theta_H/d\eta$, which gives rise to the large value of 1.86 in Fig. 4.67.

The experimentally observed value of 1.25 suggests that the Langmuir isotherm, $g = 0$, actually applies quite well for the conditions we investigated.

4.3.3 The interim conclusions for Pt electrodes

1. The o.p.d. H coverage and associated potential-dependent pseudocapacitance in the h.e.r. at Pt in acid and alkaline solutions

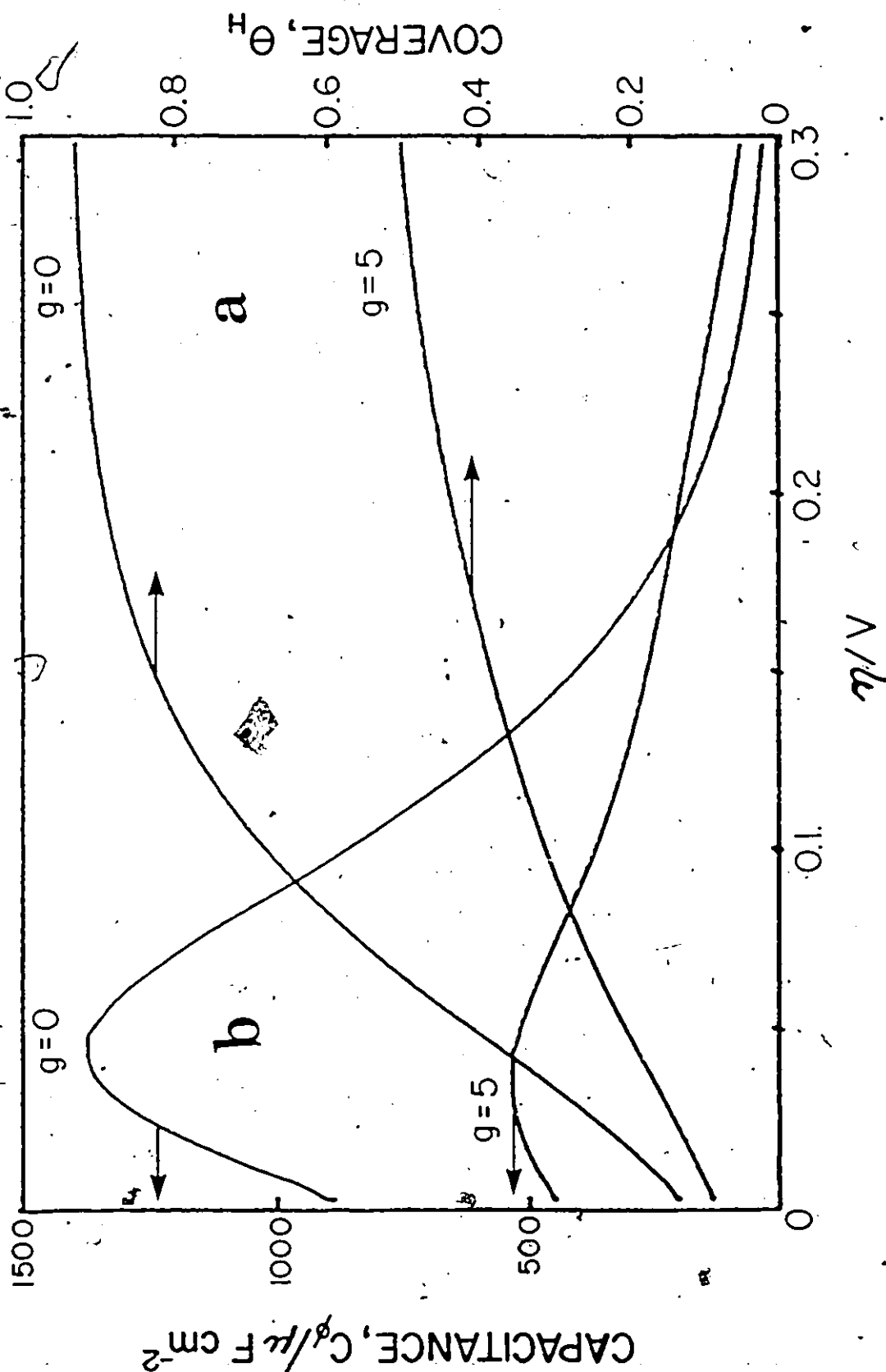


Fig. 4.66 Calculated plots of C_d and θ_H vs η in cases of $g=0$ and 5.

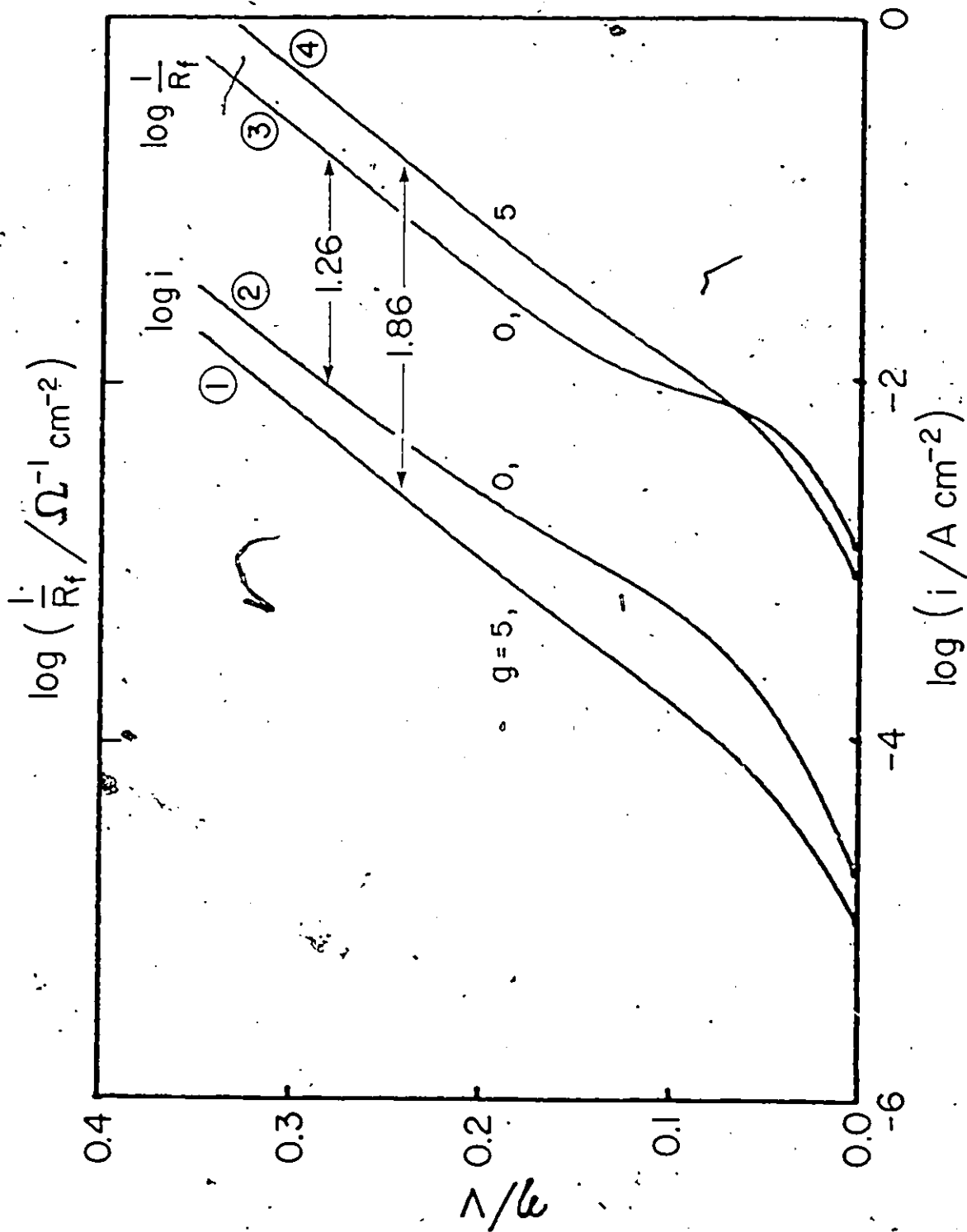


Fig. 4.67 Calculated plots of η vs $\log i$ and η vs $\log(1/R_f)$ for $g=0$ and 5.

can be evaluated from both potential relaxation and a.c. impedance experiments. The results from the above two methods are in fairly good agreement.

2. The experimentally derived H coverages can be quantitatively related to the Tafel slopes for the h.e.r. and the electrocatalytic behaviour of the reaction at Pt electrodes. The o.p.d. H coverage is much larger in acidic than in alkaline solutions.

3. The amount of o.p.d. H on Pt electrodes, which can be up to ca. 10 equivalent monolayers at activated electrodes, is related to the activity of the electrodes; the more o.p.d. H, the higher the activity. The high electrocatalytic activity for the h.e.r. at Pt is related to the formation of the extra o.p.d. H layers (perhaps a Pt-hydride surface phase), on which the M-H bond may be weakened, so that the recombination mechanism with low Tafel slope ($b = 0.036$ V) is favoured. The coverages by o.p.d. and u.p.d. H are simply related and proportional to the "active sites" on the electrodes.

4. The results indicate that the reaction mechanism of the h.e.r. at Pt is discharge step followed by the parallel recombination and electrochemical-desorption steps. The steady-state currents and coverage as a function of η can be evaluated for the above mechanism and from the rate constants which are simulated from the a.c. impedance experimental data. In general, in acid solution, the recombination step provides the major contribution to the reaction rate, especially at low η . As overpotential

increases, the electrochemical-desorption step becomes more dominant. In alkaline solution, the recombination step makes a major contribution to the reaction rate at activated electrodes, while for unactivated electrodes the discharge step becomes the rate-controlling step.

5. The mechanisms and the electrocatalytic activity of Pt for the h.e.r. are strongly dependent on the "activity" or the "cleanliness" of the electrode surface. The effects of impurities are to block the "active sites" for the discharge step, therefore reducing the extra o.p.d. H on the electrodes and retarding the recombination step. Changes of o.p.d. and u.p.d. H follow one another closely. The effects of impurities are cumulative and removable. Pt electrodes lose most of their catalytic activity (90% in acid, 99% in alkaline solution) during a period of ca. 1 h even in the rather highly purified solutions used in this work. Anodic pulsing is an effective and convenient way of reactivating poisoned Pt electrodes.

CONTRIBUTIONS TO ORIGINAL RESEARCH

1. A method for the quantitative evaluation of the behaviour of so-called "overpotential-deposited" H that is the kinetically involved chemisorbed intermediate in the cathodic H_2 evolution reaction at various metals has been developed and applied to study of the h.e.r. at Ni, Ni-Mo-Cd alloy, Au and Pt. At the latter metal, the experimentally determined behaviour of the o.p.d. H is shown to be different from that of u.p.d. H, previously well characterized.
2. A data collection and processing procedure, using a digital oscilloscope and pdp 11/34 computer for treating open-circuit potential-decay behaviour, was developed. Greatly improved accuracy is obtained compared with that in previous work employing analogue traces.
3. The improved accuracy attainable allows a new technique to be employed for handling the potential decay behaviour. Previous procedures utilize integration of the differential equation for potential decay. However, when a pseudocapacitance C_ϕ is involved, the decay equation can only be integrated after some assumption is made regarding a limiting form of C_ϕ as $f(V)$. With the new method, this is avoided by directly using the differential equation for $V(t)$, with digitally acquired data being differentiated in a computer; then the form of C_ϕ as $f(V)$ is obtained from the experimental $V(t)$ behaviour from which quantitative information on the H coverage involved during Faradaic evolution of H_2 at appreciable cathodic currents is derived.

4. The course of potential-decay was followed digitally on two Nicolet oscilloscopes used simultaneously in the circuit arrangement. By this means, digital collection of $V(t)$ information could be made over 5 ~ 6 decades of time, starting in the μs region; the dV/dt data could then be obtained accurately by numerical differentiation of the accumulated $V(t)$ data in the computer (ca. 8000 points for each decay curve).
5. The accuracy of the numerical differentiation for the experimental potential decay curve was improved by increasing the number of data points per decade (especially in the range μs to ms) and treating the data in sequential sections as a linear polynomial fitted by a simple linear regression relation using the least squares method.
6. The new potential decay method enables, for the first time, the o.p.d. H coverage to be reliably determined as a function of potential, at appreciable overpotentials, and the corresponding adsorption pseudocapacitance behaviour to be directly and accurately evaluated for the o.p.d. species in a continuous Faradaic reaction.
7. Despite a number of a.c. impedance experiments that have been reported on the behaviour of u.p.d. H and mechanisms of the h.e.r., the behaviour of o.p.d. H was for the first time determined successfully by applying the a.c. impedance method.
8. A.C. impedance spectra represented by complex-plane and Bode plots were derived for the h.e.r. at Pt, Ni and Ni-Mo-Cd plated alloy electrodes at various potentials. The behaviour is quantitatively simulated by sets of rate-constant parameters that also provide a fit of the steady-state Tafel relationships, by using a

reaction model and kinetic treatment published earlier by Armstrong and Henderson.

9. It is experimentally proved that the significance of the steady-state H adsorption pseudocapacitance is different from what is measured as the capacitance component in a.c. impedance determinations and included as a component of the commonly used 3-element equivalent circuit for representing the Faradaic impedance.

10. By means of joint use of a rotating (Pt) disc electrode technique and an "activation procedure" with a.c. impedance measurements, the "noise effect" caused by formation and removal of H_2 bubbles in the h.e.r. at Pt electrode surface was greatly reduced and the limiting diffusion process of the H_2 product moving away from the electrode at high current density (discussed in earlier works of Breiter) was avoided as well.

11. A point-by-point anodic activation procedure for study of kinetics of the h.e.r. at Pt electrodes was developed which gave excellent reproducibility. Based on this "clean surface" behaviour, the "real" kinetics of the h.e.r. and the effects of impurities at this important metal could then be studied. Attention is directed to the situation that the kinetic aspects of the mechanism of effects of impurities has not been studied previously.

12. The experimental studies show that the h.e.r. at Ni and Ni-Mo-Cd materials proceeds on a surface partially covered to a limiting extent by the adsorbed intermediate, H. Experimentally determinable limiting coverages are attained at ca. -0.15 to -0.25 V E_H and are temperature dependent.

13. The situation in (12) allows determination of the ratio of the rate constants for the rate-controlling desorption step to that for the discharge-chemisorption step.
14. Good polarization performance of the Ni-Mo-Cd electrocoated cathodes arises, in part, from the low-slope region that persists increasingly to higher current densities as the temperature is raised.
15. The low-slope region is associated with a region of high pseudocapacitance. A facile desorptive mechanism in H_2 evolution, involving this H species, which may be in the form of a surface-phase hydride, is indicated.
16. The behaviour of the Ni-Mo-Cd-coated electrodes differs in some important ways from metallic Ni and bulk Ni-Mo alloy, so the good performance of the first electrode material is not due simply to the large real-to-apparent areas, but a different reaction mechanism may be involved, that can be realized with coating procedures.
17. The experimentally derived H coverages are shown to be quantitatively related to the Tafel slopes for the h.e.r. and the electro-catalytic behaviour of the reaction at Pt electrodes. The o.p.d. H coverage is much larger in acidic than in alkaline solutions.
18. The amount of o.p.d. H on Pt electrodes, which can be up to ca. 10 equivalent monolayers at activated electrodes, is related to the activity of the electrodes: The more o.p.d. H, the higher the activity. The high electro-catalytic activity for the h.e.r. at Pt is related to the formation of the extra o.p.d. H layers (perhaps a Pt-hydride surface phase), at which the M-H bond may be weakened, so that the recombination mechanism with low Tafel slope ($b=0.036V$) is favoured.

19. The coverages by o.p.d. and u.p.d. H are simply related and proportional to the "active sites" on the electrodes.
20. The results indicate that the reaction mechanism of the h.e.r. at Pt is the proton discharge step followed by parallel recombination and electrochemical-desorption steps. The steady-state currents and coverage as a function of overpotential can be evaluated from the above mechanism and rate constants are obtained that provide a semi-quantitative simulation of the experimental a.c. impedance behaviour. In general, in acid solution, the recombination step provides the major contribution to the reaction rate, especially at low overpotentials. As overpotential increases, the electrochemical-desorption step, being potential-dependent, becomes more dominant. In alkaline solution, the recombination step makes a major contribution to the reaction rate only at activated electrodes, while for unactivated electrodes the discharge step becomes the rate-controlling step.
21. The mechanisms and the electrocatalytic activity of Pt for the h.e.r. are found to be strongly dependent on the "activity" or the "cleanliness" of the electrode surface. The effects of impurities are to block the "active sites" for the discharge step, therefore reducing the extra o.p.d. H on the electrodes and retarding the recombination step. Changes of o.p.d. and u.p.d. H, due to impurity adsorption, follow one another closely. The effects of impurities are cumulative and removable. Pt electrodes lose most of their catalytic activity (90% in acid, 99% in alkaline solution) during a period of ca. 1 h even in the rather highly purified solutions used in this work. Anodic pulsing is an effective and convenient

way of reactivating poisoned Pt electrodes.

22. ~~As~~ with u.p.d. H at Au, also no (or very little) o.p.d. H can be detected at Au electrodes either in acidic or alkaline solutions at 298K. In alkaline solution, the reaction is controlled by the discharge step, while in acidic solution, the reaction is characterized apparently by a rate-controlling "surface-diffusion" process.

23. The ~~"overlapping"~~ semi-circles in the a.c. impedance complex-plane plots were quantitatively simulated by application of a development of Armstrong's reaction model, assuming value for q_1 less than the theoretical full charge value for monolayer coverage, instead of arbitrarily decomposing them into two or more "separated" semi-circles as many other authors have done previously.

24. The apparent values of q_1 , which range from ca. 20 to 2300 $\mu\text{C cm}^{-2}$ are quantitatively related to the "active sites" for o.p.d. H species in the h.e.r. at the Pt electrode.

25. In most cases, the double-layer capacitance in the overpotential region was found to have the value of ca. $25 \pm 5 \mu\text{F cm}^{-2}$ at Ni and Pt electrodes by both potential-decay and a.c. impedance methods.

26. The situation in (25) allows determination of the real "electrochemical" surface area for the porous electrodes, which is different from that measured by the BET method, and has more significance for an electrochemical process.

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