The effect of electrolytic gas evolution on mass transfer at electrodes

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THE EFFECT OF ELECTROLYTIC GAS EVOLUTION ON MASS TRANSFER AT ELECTRODES

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Abstract - A theoretical description of a hydrodynamic model for mass transfer at gas evolving electrodes where no coalescence of gas bubbles occurs is given. To elucidate the mechanism of mass transfer, the thickness of the Nernst diffusion layer, $\delta$, has been determined as a function of the volumetric rate of the gas evolution, $v$, for both a gas evolving disc electrode and non-gas evolving ring electrodes placed concentrically around the gas evolving disc electrode. These experiments are performed for both hydrogen and oxygen evolution in alkaline solution.

It is found that for the hydrogen evolving electrode, where no coalescence occurs, the slope of the log $\delta$/log $v$ curve agrees with the theoretical slope. For the oxygen evolving electrode, where coalescence occurs frequently, the experimental and the theoretical slope differ markedly.

NOMENCLATURE

$c$  concentration of the indicator ion in the bulk of the electrolyte (mol cm$^{-3}$)
$C_w$  constant factor
$d$  diameter of a bubble (cm)
$d_b$  diameter of a bubble departing from a horizontal gas evolving electrode, i.e. break-off diameter of a bubble (cm)
$D$  diffusion coefficient of an indicator ion (cm$^2$ s$^{-1}$)
$f$  frequency of bubble emission from an active site on the electrode surface (s$^{-1}$)
$F$  Faraday constant (C mol$^{-1}$)
$g$  acceleration due to gravity (cm s$^{-2}$)
$Gr$  Grashof number ($Gr = gx^2 (\rho_f - \rho_f) w^2 \rho_i$)
$i$  current density (mA cm$^{-2}$)
$i_r$  current density of the reduction or oxidation of an indicator ion $p$ (mA cm$^{-2}$)
$k$  mass transfer coefficient (cm s$^{-1}$)
$l$  length of the electrode in the direction of the flow
$n$  number of active sites per unit surface (cm$^{-2}$)
$Nu$  Nusselt number ($Nu = k x D^{-1}$)
$Sc$  Schmidt number ($Sc = v D^{-1}$)
$T$  absolute temperature (K)
$\chi$  characteristic dimension (cm)
$U$  velocity of the solution (cm s$^{-1}$)
$v$  volumetric rate of the gas phase per unit surface, i.e. superficial velocity of the gas (cm s$^{-1}$)
$v_i$  terminal velocity of bubble rise (cm s$^{-1}$)
$z$  drag coefficient, i.e. the ratio between the volume of the liquid transported upwards by rising bubbles and the volume of the rising bubbles
$\delta$  thickness of the Nernst diffusion layer (cm)
$\rho$  mass density (g cm$^{-3}$)
$\varepsilon$  volumetric gas fraction in the bubble street of the gas evolving horizontal electrode
$\eta$  dynamic viscosity of the liquid (g cm$^{-1}$ s$^{-1}$)
$\nu$  kinematic viscosity of the liquid (cm$^2$ s$^{-1}$)

Subscripts
$g$  gas
$l$  liquid
$0$  bulk of the solution
$i$  electrode/solution interface

1. INTRODUCTION

The study of mass transfer at gas evolving electrodes is of great interest, especially for the electrochemical industry and the subject has been investigated intensively during the last 15 years.

In a recent thesis of Vogt[1] a comprehensive survey of experimental and theoretical results is given. Vogt has deduced a theoretical equation in dimensionless numbers for mass transfer at gas evolving electrodes similar to the dimensional form of Ibl and van Czemz[4-7].

In a recent paper Janssen[2] has concluded that the mass transfer can be explained on the basis of the hydrodynamic model, first proposed in 1973[3], when no coalescence of gas bubbles occurs. According to Janssen[2] the penetration model of Ibl and Venczel[4-7] may be useful when coalescence of gas bubbles occurs frequently.

In this article, the hydrodynamic model is described quantitatively. The theoretical relation between $\delta$ and the volumetric rate of gas evolution for a gas evolving electrode is compared with the experimental one for both the hydrogen and the oxygen evolving electrode in alkaline solution.

To check the conclusions about the mechanism of mass transfer at gas evolving electrodes, $\delta$ is determined at ring electrodes placed concentrically to a gas evolving disc. The solution flow induced by ascending gas bubbles determines $\delta$ at the ring electrodes. Moreover, the relation between $\delta$ at the ring electrode and $\delta$ at the gas evolving electrode is determined.

2. EXPERIMENTAL

2.1 Electrolytic cell

A normal H-type electrolytic cell divided into two compartments separated by an ion-exchange membrane (Nafion 425) was used. A diagram of this cell.
Fig. 1. Schematic diagram of the experimental cell.

with pertinent dimensions is given in Fig. 1. The horizontal test-electrode (dia 4.0 cm) served as a part of the bottom of the test-compartment. The electrolytic cell was thermostated; the temperature of the electrolyte was usually 25°C.

2.2 Electrodes

Two different types of electrode, A and B, were used. Both types of electrode consisted of a nickel disc of about 0.8 cm dia surrounded concentrically by nickel rings of different surface area. The disc and the rings were separated from one another by an insulating material of a thickness of about 0.006 cm (Fig. 1).

For electrode A the surface area of the disc was 0.51 cm², that of the inner ring 0.35 cm², and that of the outer ring 4.07 cm². The width of the inner ring was 0.115 cm and that of the outer ring 0.72 cm. For electrode B the surface area of the disc was 0.55 cm², that of the inner ring 1.79 cm², that of the middle ring 2.98 cm² and that of the outer ring 4.36 cm². The width of all of these three rings was about 0.4 cm. A diagram of electrode B is shown in Fig. 1.

2.3 Electrolyte and analysis

A 1 M KOH solution was used as supporting electrolyte, unless otherwise mentioned. For the experiments with the hydrogen evolving electrode the solution was made 0.03 M in K₃Fe(CN)₆. For the experiments with the oxygen evolving electrodes the 1 M KOH solution contained 0.03 M K₄Fe(CN)₆.

When, however, the thickness of the diffusion layer at the non-gas evolving electrodes had to be determined, the alkaline solution was made 0.03 M in K₃Fe(CN)₆. The use of these different indicator ions was preferred because of the small difference between the normal potential of the Fe(CN)₆⁴⁻/Fe(CN)₄⁻ redox couple and that of the O₂/OH⁻ redox couple in 1 M KOH. The quantity of Fe(CN)₆⁴⁻ formed during the oxygen evolution was determined by titration with Ce⁴⁺ [8].

2.4 Procedure

Usually, the following procedure was applied in determining the thickness of the Nernst diffusion layer at a gas evolving electrode.

Before each experiment in a series, the test electrode was polarized in the supporting electrolyte for 15 min at a current density equal to that of the experiment. After the 15 min pre-polarization a calculated quantity of the indicator ion was added.

Usually 10 ml 0.63 M K₃Fe(CN)₆ or K₄Fe(CN)₆ was added to 175 ml supporting electrolyte.

The determination started without interrupting the current at the addition of the indicator ion.

During a series of experiments the determinations were performed in a sequence of decreasing current density. The decrease in the concentration of the indicator ion was about 2%.

In a number of experiments, however, the current was just switched on at the moment of addition of the indicator ion.

The thickness of the diffusion layer at the non-gas evolving ring electrodes was obtained by measuring the current used for the reduction of Fe(CN)₆⁴⁻ for all experiments.

For the experiments with the hydrogen and the oxygen evolving electrodes, the potential of one or all the non-gas evolving ring electrodes was maintained potentiostatically at −500 mV and −300 mV vs sce, respectively. At these potentials the oxidation of hydrogen was negligible and the limiting diffusion current for the reduction of Fe(CN)₆⁴⁻ was attained. The current at the gas evolving electrode, however, was adjusted galvanostatically. For 3 min this electrode was polarized with a constant current density. During this period the current at the non-gas evolving electrode was recorded. The average current for the last minute of this period was determined.

Usually a series of experiments started with the highest current density; the current at the disc was decreased in steps. After measurements with decreasing current density, measurements with increasing current density were carried out in a limited number of experiments. The results were practically the same.

3. RESULTS

3.1 Introduction

The thickness δ of the Nernst diffusion layer is calculated from the well-known equation:

$$\delta = \frac{FDc}{lp}.$$  

For the calculation of δ the diffusion coefficient of Fe(CN)₆⁴⁻ vs 7.0 × 10⁻⁶ cm²/s at 25°C and that of Fe(CN)₄⁻ 7.9 × 10⁻⁶ cm²/s at 25°C were used[3]. Taking into account the activation energy of the diffusion coefficient of the indicator ion in 1 M KOH[9] and the viscosity of KOH solutions[10] the diffusion coefficients of the indicator ions at different temperatures and solutions with different KOH concentrations were calculated. The thickness of the diffusion layer at both the gas evolving electrode and the non-gas evolving electrodes was usually deter-
determined as a function of the current density used for the gas evolution. In the next section relations between $\delta$ and $i_0$, or $i_{H_2}$, are given.

### 3.2 Hydrogen evolution

The bubbles ascending from the disc electrode induce an electrolyte flow in the cell. This flow also passes the ring electrodes mounted concentrically around the gas evolving disc electrode.

In the following the influence of the rate of the hydrogen evolution upon the limiting rate of mass transfer at the non-gas evolving electrodes is shown.

In Fig. 2, log $\delta$ at both rings of electrode A is plotted vs log $i_{H_2}$ at the disc, when the rings are polarized separately at $-500$ mV. The current density $i_{H_2} = i - i_{Fe(CN)}^3$-$$. For the experiments where both rings of electrode A where polarized simultaneously, it was found that the slopes of the log $\delta$/log $i_{H_2}$ curves were equal to those of Fig. 2. $\delta$ for the outer ring was equal to that of Fig. 2 and $\delta$ for the inner ring was a factor 1.8 greater than that of Fig. 2.

The results for electrode B at separate polarization of the ring electrodes are represented in Fig. 3. This figure shows that $\delta$ increases with increasing distance between the ring and the gas evolving disc electrode. From experiments with separate and with simultaneous polarization, it was found that for simultaneous polarization, $\delta$ at the inner and the middle ring reaches a higher value and $\delta$ at the outer ring equals the value obtained at separate polarization. This result can be explained by the decrease of the $Fe(CN)^3$-$ concentration in the electrolyte flowing past the outer ring. It was also determined for the inner ring of electrode A when the hydrogen evolution occurred with the same current density at both the outer ring and the disc.

Additional hydrogen evolution at the outer ring had a small influence upon $\delta$ at the inner ring, viz at $i_{H_2} = 100$ mA/cm$^2$, $\delta$ decreased about 15% and the slope of the log $\delta$/log $i_{H_2}$ curve increased about 50%.

The influence of temperature upon $\delta$ at the inner ring of electrode A, at a constant volumetric rate of hydrogen and water vapour formation on the disc electrode, was determined. It appeared that in the investigated temperature range from 25 to 70°C (and at a volumetric rate of hydrogen and water vapour
formation of 0.77 ml/min cm², corresponding with a hydrogen evolution of 200 mA/cm² at 25°C, the temperature has practically no influence upon δ. The effect of the KOH-concentration upon δ was also investigated at the inner ring of electrode A at 25°C and at a hydrogen evolution of 40 mA/cm² on the disc. Solutions of 1, 2, 3 and 4 M KOH containing 0.03 M K₄Fe(CN)₆ were used.

It appeared that δ increased slightly with increasing KOH-concentration; δ at 4 M KOH is about 20% larger than δ at 1 M KOH.

For the hydrogen evolving disc electrode log δ/log iₐ, curves are plotted in Fig. 4. This figure shows also the influence of the 15 min pre-polarization of the disc electrode. The experiments were started at the highest current density. In both experiments at iₐ > 1.5 A/cm² coalescence of hydrogen bubbles occurred very frequently.

3.3 Oxygen evolution

During oxygen evolution at the disc electrode, the reduction current of Fe(CN)₆³⁻ at the ring electrode fluctuated little at current densities for the disc electrode, i₀₂ < 80 mA/cm², but intensively at higher current densities, i₀₂ > 80 mA/cm².

The change occurred rather abruptly and was not observed with hydrogen evolution. This abrupt change may be caused by the sudden occurrence of frequent coalescence of oxygen bubbles at i₀₂ = 80 mA/cm².

In the following the influence of the rate of oxygen evolution upon δ of the ring electrodes is shown. In Fig. 5, log δ at the two rings of electrode A is plotted vs log i₀₂ at the disc for separate polarization of both rings at −300 mV. The results for electrode B are given in Fig. 6, which shows that δ also increases with increasing distance between ring and gas evolving disc for separate polarization of the ring electrodes.

The effect of the simultaneous polarization of the ring electrodes upon δ was the same as with the hydrogen evolving electrodes.

δ was also determined at the inner ring of electrode A for simultaneous oxygen evolution at both the disc and the outer ring with the same current density. The additional oxygen evolution at the outer ring decreased δ at the inner ring with about 30%.

For the investigated current density range from 10 to 400 mA/cm² the slope of the relation between log δ at the inner ring and log i₀₂, at the disc and at the outer ring is equal to that at i₀₂ < 80 mA/cm², Fig. 5.

The relation between log δ and log i₀₂ for the gas evolving disc electrode A is represented in Fig. 7. In this case, Fe(CN)₆³⁻ was used as indicator ion and was oxidized at the limiting current density.

For the oxygen evolving electrode i₀₂ = i - iₐFe(CN)₆³⁻. The log δ/log i₀₂ curve of Fig. 7 has an intersection point at about 20 mA/cm². At high current densities, viz i₀₂ > 20 mA/cm², the slope is much steeper than those of the curves of Figs 5 and 6.

4. THEORY

A gas bubble is initiated on an active site of the electrode, and grows by absorption of gas from the surrounding supersaturated solution. Upon detachment each ascending gas bubble transports upwards a quantity of solution.

At steady state the volume of the liquid transported upwards is equal to the volume of the liquid which flows downwards. The velocity distribution of the latter flow depends on many factors, such as the dimensions of the electrolytic cell and of the gas evolving electrode, the position of the gas evolving electrode, the volumetric rate of the gas evolution, the size of the ascending bubbles and the viscosity of the liquid. The electrolyte flow induced by ascending bubbles strongly affect each other, and the trajectory of the ascending bubble.

The hydrodynamic model introduced by Janssen and Hoogland[3] is based on the liquid flow induced by ascending gas bubbles. This flow can be compared with the free-convection flow induced by differences in density of the electrolyte.

For both turbulent and laminar free-convection flow, experimental as well as theoretical relations have been found for mass transfer at both vertical and horizontal electrodes[11-14]. However, an exact or even approximate theoretical treatment of the hydrodynamic model of Janssen and Hoogland for the mass transfer is not available. Only some experimental relations for related systems have been obtained.
Ibl et al. [15, 16] have investigated mass transfer at 
vertical electrodes when gas bubbles were sparged by 
porous frits at the bottom of the electrolytic cell into 
the electrolyte. A great part of these gas bubbles ascend 
in the vicinity of the vertical electrode. Weder [17] 
studied mass transfer at a horizontal electrode where 
gas was bubbled through a hole in the centre of the 
electrode.

Free-convection flow due to differences in density of 
the liquid is turbulent for disc electrodes with dia-
meters greater than about 1–2 cm [11]. For this turbu-
 lent flow the mass transfer rate at the electrode is given 
by [11],

\[ Nu = 0.15(Gr \cdot Sc)^{1/3}, \]

(1)

Substitution of \( k/D \) by \( \delta \), the thickness of the Nernst 
diffusion layer, gives

\[ \delta = 6.7 \left( \frac{\rho g D}{(\rho_0 - \rho_l)g} \right)^{1/3}. \]

(2)

For free-convection flow, resulting from differences in 
density of the liquid, the buoyancy force per unit mass is

\[ \left( \frac{\rho_0 - \rho_l}{\rho_l} \right) g. \]

For reasons of analogy we considered a horizontal gas 
evolving disc electrode. In this case the convection flow 
is only caused by the lift effect of ascending gas 
bubbles.

Assuming that both the volumetric gas fraction, \( e \), in 
the bubble street and the drag coefficient, \( z \), are 
independent of the height above the electrode surface, 
the buoyancy factor per unit mass is:

\[ (z \varepsilon \rho_l) \frac{([1 - e] \rho_l + e \rho_g)}{\rho_l}. \]

This factor is similar to the buoyancy factor resulting 
differences in density of the solution.

Consequently, the factor \( (\rho_0 - \rho_l) \rho_l \) in (2) is 
replaced by

\[ z \varepsilon \rho_l \frac{([1 - e] \rho_l + e \rho_g)}{\rho_l}. \]

This gives the following expression for \( \delta \)

\[ \delta = C_1 \left( \frac{v \varepsilon \rho_l}{z \varepsilon \rho_1} \right)^{1/3}. \]

(3)

The detached bubbles rise in a swarm and induce a 
liquid flow. This flow affects both the trajectory and 
the velocity of each bubble. Assuming an equal size of 
all the bubbles the relation between the superficial 
velocity of the gas – the volumetric rate, \( \varepsilon \), of the 
gas phase per unit of surface area – and the volumetric 
gas fraction, \( e \), is given [18] by

\[ v = v_1 \left( \frac{e}{1 - e} \right). \]

(4)

In this equation \( v_1 \) is the terminal velocity of a single 
bubble in an infinite medium and is equal to

\[ v_1 = \frac{1}{12 g d^2 (\rho_1 - \rho_g) \eta_1}. \]

(5)

Rietema et al. [18] studied a system similar to a gas 
evolving horizontal electrode.

Relation (4) is also found for a “turbulent” regime of 
ascenting bubbles [19]. This regime is characterized 
by large liquid convection induced by ascending 
bubbles. The “turbulent” regime, mentioned in the 
literature, is associated with bubble coalescence. How-
ever, we consider now a regime where no coalescence 
of bubbles occurs. This should be well compared with a 
“laminar” regime as defined by Zuber [19]. In contrast 
to our bubble system, however, in the system with 
“laminar” flow, the liquid ahead of and behind rising 
bubbles is at rest; no gross liquid circulation exi-
sts [19]. For the “laminar” regime Zuber gives

\[ v = \frac{v_1 e (1 - e)}. \]

(6)

At low volumetric gas fractions \( v \) is practically equal to 
\( v_1 e \) for both regimes of the bubble system.

Owing to the influence of liquid flow upon the 
behaviour of bubbles, (4) for the relation between \( v \) and 
\( e \), is preferable.

Taking into account \( \rho_1 \ll \rho_1 \) substitution of (4) into 
(3) gives

\[ \delta = C_1 \left( \frac{v \varepsilon \rho_l}{z \varepsilon \rho_1} \right)^{1/3}. \]

(7)

Assuming the drag coefficient \( z \) does not depend on \( v \), 
from (7) it can be deduced that the log \( \delta / \log v \) curve is 
straight with a slope of \( -0.33 \).

For a population density, \( n \), of active sites on the 
electrode, a frequency, \( f \), of bubble emission at an 
active site and a break-off diameter, \( d_b \), the volumetric 
rate of gas evolution per unit of surface area is

\[ v = \frac{1}{6 \pi d_b^3 n f}. \]

(8)

From (6) and (7) it follows after substitution of \( \rho_1 \) 
- \( \rho_1 \)/n \( \approx \rho_1/n \approx v \) that

\[ \delta = C_2 \left( \frac{D}{z \varepsilon \rho_1} \right)^{1/3}. \]

(9)

If the uniform bubble diameter \( d_b \) depends on \( v \), it is 
likely also that the parameters \( z, n \) and \( f \) depend on \( v \). 
The relation between \( \delta \) and \( v \) is then complex.

Zuber [19] has deduced a relation for heat transfer 
per unit mass at a horizontal surface at which nuclear 
boiling occurs. Owing to the analogy between heat and 
mass transfer the relation of Zuber can be transformed 
into a relation for mass transfer. In this case only the effect 
of bubbles is taken into account. After substitution of 
various parameters by the analogues for mass transfer 
we obtain (and assuming \( \rho_1 \ll \rho_1 \))

\[ \frac{k d}{D} = C_3 \left( \frac{u d B_v}{v D} \right)^{1/3}. \]

(10)

Substitution of \( k \) by \( D/\delta \) and rearrangement of (10) 
gives

\[ d = C_4 \left( \frac{v D}{g e} \right)^{1/3}. \]

(11)

As mentioned earlier, \( \varepsilon = e/v_1 \) at low gas fractions. 
From this relation and (11) it follows that

\[ \delta = C_4 \left( \frac{v D e}{g e} \right)^{1/3}. \]

(12)
Comparison of this equation for $\delta$ with (7) shows that both equations for $\delta$ are equal if $C_1 = C_2 z^{-1/3}$.

5. DISCUSSION

During both the hydrogen and the oxygen evolution at the disc electrode a circulation flow of the solution occurs in the electrolytic cell. The rate of this flow increases with increasing rate of gas evolution. Due to this increasing flow rate $\delta$ decreases at the ring electrodes, placed concentrically around the gas evolving disc electrode.

Assuming that the effect of the edges can be neglected, the thickness $\delta$ of the Nernst diffusion layer according to Levich for a plate electrode in laminar flow is [20]

$$\delta = 1.47D^{1/2} \rho^{1/2} v^{1/6} U^{-1/2}. \quad (13)$$

The solution flow velocity $U$ at the inner ring of electrode A is calculated for hydrogen evolution of 1 A/cm$^2$ at the disc of electrode A at 25°C and in 1 M KOH as supporting electrolyte. The kinematic viscosity of 1 M KOH at 25°C is 0.01073 cm$^2$/s, the diffusion coefficient of Fe(CN)$_6^{3-}$ in 1 M KOH at 25°C is $7.9 \times 10^{-6}$ cm$^2$/s and the width of the inner ring is 0.115 cm. Figure 2 shows that $\delta$ at the inner ring for $i_{H_2} = 1$ A/cm$^2$ is 7.5 $\times 10^{-3}$ cm.

Calculation with (13) gives $U = 0.38$ cm/s. With $Re = U l / v$, $Re$ is about 4. From this very low value for $Re$ it follows that the flow in the neighbourhood of the ring electrodes is laminar.

Figures 2 and 3 show that for experiments with the hydrogen evolving disc electrode all the curves of the plots of $\log \delta$ at the ring electrode vs $\log i_{H_2}$ at the disc electrode, are practically parallel to one another. Moreover, the slope of these curves is of the order of magnitude of those of the $\log \delta / \log i_{H_2}$ curve for the disc electrode.

From the experiments with electrode B it is found that $\delta$ at the inner ring is smaller than $\delta$ at both other rings for individual polarization of the rings (Fig. 3). The width of the rings of electrode B are nearly equal. Consequently, $\delta$ at the ring electrodes increases with increasing distance from the gas evolving disc electrode. This conclusion is supported by the experiments with electrode A (Fig. 2). The results of the experiments with oxygen evolution at $i_{O_2} < 20$ mA/cm$^2$ support the conclusions deduced from those with hydrogen evolution. However, for oxygen evolution at $i_{O_2} > 20$ mA/cm$^2$ the results of Figs 5 and 6 and that of Fig. 7 are completely different. In this current density range coalescence of oxygen bubbles occurs very frequently.

In the following the experiments with $i_{O_2} > 20$ mA/cm$^2$ are discussed. The $\log \delta / \log i_{O_2}$ curve at the gas evolving disc electrode (Fig. 7) is much steeper than the curves for the relation between $\log \delta$ at the ring electrode and $\log i_{O_2}$ at the disc electrode (Figs 5 and 6).

Even $\delta$ at the inner ring of electrode A remains practically constant with increasing rate of oxygen evolution at the disc of electrode A. The $\log \delta / \log i_{O_2}$ curve at the gas evolving disc electrode agrees with those mentioned in the literature [2, 3].

From the preceding discussion it follows that there is only an evident correlation between $\delta$ at the ring electrodes and $\delta$ at the gas evolving disc electrode if no coalescence of gas bubbles occurs. The thickness of the diffusion layer at a gas evolving electrode is then determined by the solution flow at the electrode which is induced by ascending gas bubbles. Incorporating this solution flow is basic to the hydrodynamic model introduced by Janssen and Hoogland [3].

The hydrogen evolving electrode at $1 \text{ mA/cm}^2 < i_{H_2} < 100 \text{ mA/cm}^2$ in alkaline solution generates bubbles with a practically constant diameter [3]; coalescence of bubbles does not occur. Though no measurements at $i_{H_2} > 100 \text{ mA/cm}^2$ are known, the observed dependency of $\delta$ on $i_{H_2}$ at a hydrogen evolving electrode (Fig. 4) tends to the conclusion that it is likely that at $100 \text{ mA/cm}^2 < i_{H_2} < 1 \text{ A/cm}^2$ practically no coalescence of hydrogen bubbles occurs.

The experimental slope of the $\log \delta / \log i_{H_2}$ curve at the hydrogen evolving disc electrode is about $-0.32$ (Fig. 7). This value agrees with earlier results [2, 3].

For the hydrodynamic model presented in Section 4 the theoretical slope of the $\log \delta / \log v$ curve is equal to $-0.33$ at a constant uniform bubble size. Taking into consideration the assumptions made, there is a good agreement between the experimental and the theoretical slope. Consequently, the hydrodynamic model describes the mass transfer at a gas evolving electrode at which no coalescence of bubbles occurs very well.

The assumptions about the size of bubbles is supported by new experimental results [21].

The bubbles formed at a hydrogen evolving electrode at which no coalescence of bubbles occurs can be divided into two groups, viz small bubbles forming part of a bubble train departing from an active site, and large single bubbles which grow during a relatively long time and then detach individually from the electrode.

For a hydrogen evolving electrode in alkaline solution the distribution of active sites and the ratio of large single bubbles depend on the time of polarization. At the beginning of the polarization relatively numerous single bubbles are formed and this number decreases with increasing time of polarization. In the steady state only small bubbles occur which become incorporated into bubble trains. These small bubbles have a near-uniform size, which is almost independent of current density.

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